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# Analysis of Random Errors in Air-Quality Measurements

Radian Corp, Austin, Tex

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# ANALYSIS OF RANDOM ERRORS IN AIR-QUALITY MEASUREMENTS

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FINAL REPORT

U.S. ENVIRONMENTAL PROTECTION AGENCY
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An analysis has been performed of the random errors involved in measurements of ozone, $SO_2$, NO, and $NO_x$ made with the Radian-built air-monitoring trailers. Differences observed between "known" test gas concentrations and the corresponding machine responses were used to quantify the error properties. Data obtained through quality-assurance audits, performed both by EPA and Radian, and through daily autocalibrations of the instrumentation were analyzed.

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# ANALYSIS OF RANDOM ERRORS IN AIR-QUALITY MEASUREMENTS

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## TABLE OF CONTENTS


| | | Page |
|---|---|---|
| | ACKNOWLEDGEMENTS---------- | vii |
| | EXECUTIVE SUMMARY---------- | viii |
| 1.0 | INTRODUCTION---------- | 1 |
| 2.0 | ANALYSIS OF AUDIT DATA---------- | 4 |
| 3.0 | ANALYSIS OF ZERO-SPAN DATA---------- | 17 |
| 4.0 | SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS------ | 32 |
| | REFERENCES---------- | 35 |
| APPENDIX A - | TESTS OF THE NORMALITY OF THE RANDOM ERRORS---------- | 36 |
| APPENDIX B - | PROPOSED EXPERIMENTAL DESIGN FOR FOLLOW-UP STUDY---------- | 45 |
| APPENDIX C - | SEPTEMBER, 1976, ZERO-SPAN AUTOCALIBRATION DATA---------- | 52 |

## LIST OF TABLES


| | | Page |
|---|---|---|
| 2-1 | Standard Deviations by Auditing Agency (ppm)---------- | 6 |
| 2-2 | Pooled Standard Deviations (ppm)---------- | 8 |
| 2-3 | Decision Rule for Testing Consistency Between Audit Point and Machine Response (Ozone)---------- | 10 |
| 2-4 | Statistics on Random Errors* in Ozone Audit Points: All Instruments, All Dates, Concentrations in ppm---------- | 13 |
| 2-5 | Statistics on Random Errors in $SO_2$ Audit Points: All Instruments, All Dates, Concentrations in ppm---------- | 14 |
| 2-6 | Statistics on Random Errors in NO Audit Points: All Instruments, All Dates, Concentrations in ppm---------- | 15 |
| 2-7 | Statistics on Random Errors in $NO_x$ Audit Points: All Instruments, All Dates, Concentrations in ppm---------- | 16 |
| A-1 | Skewness and Kurtosis Statistics (Ozone)------- | 41 |
| A-2 | Skewness and Kurtosis Statistics ($SO_2$)-------- | 42 |
| A-3 | Skewness and Kurtosis Statistics ($NO_x$)--------- | 43 |
| A-4 | Skewness and Kurtosis Statistics (NO)---------- | 44 |
| C-1 | Four-Day Mean Value of Machine $O_3$ Sensor Respone to Zero Gas Versus Time Since Last Multi-Point Calibration---------- | 53 |
| C-2 | Four-Day Standard Deviation of Machine $O_3$ Sensor Response to Zero Gas Versus Time Since Last Multi-Point Calibration---------- | 54 |

## LIST OF TABLES (Cont'd)


| | | Page |
|---|---|---|
| C-3 | Four-Day Mean Value of Span Gas Concentration Minus Machine $O_3$ Sensor Response Versus Time Since Last Multi-Point Calibration---------- | 55 |
| C-4 | Four-Day Standard Deviation of Span Gas Concentration Minus Machine $O_3$ Sensor Response Versus Time Since Last Multi-Point Calibration---------- | 56 |
| C-5 | Four-Day Mean Value of Machine $SO_2$ Sensor Response to Zero Gas Versus Time Since Last Multi-Point Calibration---------- | 57 |
| C-6 | Four-Day Standard Deviation of Machine $SO_2$ Sensor Response to Zero Gas Versus Time Since Last Multi-Point Calibration---------- | 58 |
| C-7 | Four-Day Mean Value of Span Gas Concentration Minus Machine $SO_2$ Sensor Response Versus Time Since Last Multi-Point Calibration---------- | 59 |
| C-8 | Four-Day Standard Deviation of Span Gas Concentration Minus Machine $SO_2$ Sensor Response Versus Time Since Last Multi-Point Calibration---------- | 60 |
| C-9 | Four-Day Mean Value of Machine $NO_x$ Sensor Response to Zero Gas Versus Time Since Last Multi-Point Calibration---------- | 61 |
| C-10 | Four-Day Standard Deviation of Machine $NO_x$ Sensor Response to Zero Gas Versus Time Since Last Multi-Point Calibration---------- | 62 |
| C-11 | Four-Day Mean Value of Span Gas Concentration Minus Machine $NO_x$ Sensor Response Versus Time Since Last Multi-Point Calibration---------- | 63 |
| C-12 | Four-Day Standard Deviation of Span Gas Concentration Minus Machine $NO_x$ Sensor Response Versus Time Since Last Multi-Point Calibration---------- | 64 |
| C-13 | Dates of Multi-Point Calibrations Performed in September, 1976---------- | 65 |

## LIST OF FIGURES


| | | Page |
|---|---|---|
| 3-1 | Four-Day Mean Value of Machine $O_3$ Sensor Response to Zero Gas Versus Time Since Last Multi-Point Calibration-------- | 20 |
| 3-2 | Four-Day Standard Deviation of Machine $O_3$ Sensor Response to Zero Gas Versus Time Since Last Multi-Point Calibration-------- | 21 |
| 3-3 | Four-Day Mean Value of Span Gas Concentration Minus Machine $O_3$ Sensor Response Versus Time Since Last Multi-Point Calibration---------- | 22 |
| 3-4 | Four-Day Standard Deviation of Span Gas Concentration Minus Machine $O_3$ Response Versus Time Since Last Multi-Point Calibration---------- | 23 |
| 3-5 | Four-Day Mean Value of Machine $SO_2$ Sensor Response to Zero Gas Versus Time Since Last Multi-Point Calibration---------- | 24 |
| 3-6 | Four-Day Standard Deviation of Machine $SO_2$ Sensor Response to Zero Gas Versus Time Since Last Multi-Point Calibration---------- | 25 |
| 3-7 | Four-Day Mean Value of Span Gas Concentration Minus Machine $SO_2$ Sensor Response Versus Time Since Last Multi-Point Calibration-------- | 26 |
| 3-8 | Four-Day Standard Deviation of Span Gas Concentration Minus Machine $SO_2$ Sensor Response Versus Time Since Last Multi-Point Calibration---------- | 27 |
| 3-9 | Four-Day Mean Value of Machine $NO_x$ Sensor Response to Zero Gas Versus Time Since Last Multi-Point Calibration---------- | 28 |
| 3-10 | Four-Day Standard Deviation of Machine $NO_x$ Sensor Response to Zero Gas Versus Time Since Last Multi-Point Calibration---------- | 29 |

## LIST OF FIGURES (Contd)


| | | Page |
|---|---|---|
| 3-11 | Four-Day Mean Value of Span Gas Concentration Minus Machine $NO_x$ Sensor Response Versus Time Since Last Multi-Point Calibration---------- | 30 |
| 3-12 | Four-Day Standard Deviation of Span Gas Concentration Minus Machine $NO_x$ Sensor Response Versus Time Since Last Multi-Point Calibration---------- | 31 |

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## EXECUTIVE SUMMARY

An analysis has been performed of the random errors involved in measurements made with the Radian-built air-monitoring trailers. Observed differences between "known" test gas concentrations and corresponding machine responses were used to quantify the error properties.

The statistical properties of the errors observed in quality assurance audits are described, and a decision rule is presented for determining whether an ozone audit test gas sample and the ozone sensor response are consistent within normally expected random variations. The random errors in $SO_2$, NO, and $NO_x$ audits are also described in quantitative terms. It is recommended, however, that the variations in error properties depending on the audit-performing agency be investigated further before formal decision rules are derived for these other pollutants.

The random variations in the daily autocalibration process were also analyzed. No evidence of a long-term systematic drift or of any trailer-dependent bias was observed. The data used in the autocalibration process fall within definable limits when there is no malfunction and usually fall far outside these limits when there is a malfunction. Thus, the daily autocalibration data appear to be good indicators of a system malfunction.

Recommendations, including a list of physical questions to be answered and a proposed experimental design, are presented for a follow-up study which would verify and extend the results of this project.

## 1.0 INTRODUCTION

The purpose of this study, stated in broad terms, is to describe in quantitative terms the nature of the random errors involved in pollution measurements made with the Radian-built air-monitoring trailers. The uncertainties impact the use of the measurements in some important ways, as is discussed in more detail later in this chapter.

The data used in this study were collected between May and October of 1976, in connection with another project performed for the Environmental Protection Agency. The ambient concentrations of ozone, $SO_2$, NO, and $NO_x$ were measured continuously at nine sites in Louisiana during the project. These and other data collected and the equipment used are described in Reference 3.

The use of only Radian trailer data in this study was necessitated by the following two considerations:

(1) There were insufficient funds available to collect and examine a large sample of data from several agencies.

(2) In the initial effort it was considered desirable to eliminate, to the extent possible, variations in results due to variation in operator procedures and equipment. Therefore, since Radian trailers used in the Louisiana study were all of the same type, and all operators were trained by Radian, it was believed that selection of Radian trailer data would minimize extraneous influences.

While it is not the purpose of this report to present a detailed treatment of the trailer instrumentation or operation, the following brief discussion of certain relevant aspects of operation is included for completeness.

Each trailer was recalibrated at about one-month intervals. Recalibration, for each pollutant measured, consists of obtaining the machine measurements corresponding to test gas samples with a range of known concentrations. Thus, a correspondence, assumed to be linear, can be established between the machine reading in volts and the pollutant concentration.

Between calibrations, daily "zero" and "span" checks are made, so that drifts can be accounted for. This consists of (1) obtaining the machine response for each pollutant to a pollution-free gas sample and to a "span" gas sample, which has a preselected concentration between 50 and 500 parts per billion and (2) making the necessary correction in the correspondence between the electronic measurement in volts and pollutant concentration. The one exception is that the ozone span gas is not used for daily corrections, since the daily variations in the measuring characteristics are believed to be somewhat less than the random error in ozone span gas generation.

At periodic times during the Louisiana study, audits were performed by EPA or by Radian. An audit involves simply a check on the consistency between the known concentrations of a set of test gas samples and the corresponding measurements.

The objective of this study, then, is to quantify the measurement errors as revealed by the discrepancies between test gas concentration and machine response. Both audit and zero-span data were used for this purpose. The actual errors analyzed inevitably involve random variations both in the measurement process and in test gas concentration.

The calibration points are not as useful for error analysis, since readjustments are made to the equipment as the calibration is performed. Thus, interpretation of the differences between test gas concentration and machine response is nebulous.

The error analyses presented herein are intended to be used as:

(1) an aid in deciding whether an audit test gas concentration is consistent with machine response within normally expected random variations,

(2) to assess the usefulness of zero-span data in evaluating machine accuracy and possibly for determining the need for a quality assurance audit or recalibration, and

(3) as a general aid in interpreting the air pollution measurements in light of the inevitable random variations.

## 2.0 ANALYSIS OF AUDIT DATA

In this section, the analyses of the audit errors are presented. The objective is to characterize the random variations which normally occur when the equipment is performing correctly, that is, when there is no malfuntion.

For this reason, audits performed when there were known mechanical problems were excluded, as were audits with large errors (over 20%) performed when the zero-span data also indicated a severe drift or other error which clearly exceeded normal day-to-day fluctuations. On these bases, five out of 75 audits for $SO_2$ and 13 out of 82 simultaneous NO and $NO_x$ audits were rejected. In the case of the NO and $NO_x$ audits, a large common error (such as +40% for one and +42% for the other) was another likely indication of an abnormality such as a large error in the concentration of the common test gas stream for NO and $NO_x$ or a malfunction in one of the hardware components, such as the vacuum pump, which affect both NO and $NO_x$ measurements.

None of the ozone audit points were rejected. The much newer condition of the ozone equipment probably explains the relative absence of malfunctions in the ozone equipment. The ozone sensors were new and the other equipment was about two years old at the beginning of the project.

### Analysis of Random Variations in Audit Results

Table 2-1 presents the standard deviations of the quantity, machine response minus test gas concentration, for various situations. The standard deviation is a measure of the amount of variability in a set of points, and is defined by:

$$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}}$$

where

$x_i$, i = 1 to N, is the set of points and $\bar{x}$ is the mean of the x's.

The integer N - 1 is referred to as the number of "degrees of freedom" in this estimate of the standard deviation and is used in certain statistical calculations to be discussed which involve the t statistic.

If the errors have the normal distribution, then in an individual case, the probability is .68 (about 2/3) that an error in an individual case falls within plus and minus one standard deviation of its mean; thus, the standard deviation represents a larger than average case-to-case variation.

The applicability of the normal distribution, as a reasonable approximation of the error distribution, is discussed in Appendix A.

In light of the above, then, Table 2-1 quantifies the random effects observed in the auditing process.

It can be seen that the standard deviations generally increase as the test gas concentration increases, although this effect does not occur in every instance.

## TABLE 2-1

## STANDARD DEVIATIONS BY AUDITING AGENCY (PPM)

| Test Gas Concentration | Agency | Ozone | | $SO_2$ | | NO | | $NO_x$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | s | d.f. | s | d.f. | s | d.f. | s | d.f. |
| .4-.5 | EPA | .018 | 3 | .051 | 8 | .035 | 5 | .028 | 3 |
| .4-.5 | Radian | .041* | 32 | - | - | .049 | 3 | .059 | 3 |
| .3-.4 | EPA | .041 | 15 | .077 | 22 | .044 | 13 | .025 | 11 |
| .3-.4 | Radian | .039 | 15 | .057 | 25 | .055 | 22 | .056* | 20 |
| .2-.3 | EPA | .034 | 31 | .058* | 21 | .046* | 26 | .018 | 17 |
| .2-.3 | Radian | .030 | 35 | .034 | 15 | .017 | 7 | .022 | 7 |
| .1-.2 | EPA | .018 | 33 | .033 | 30 | .025 | 43 | .014 | 30 |
| .1-.2 | Radian | .017 | 11 | .024 | 34 | .019 | 48 | .019 | 46 |
| 0-.1 | EPA | .014 | 12 | .017* | 1 | .019 | 7 | .020 | 6 |
| 0-.1 | Radian | - | - | .005 | 9 | .008 | 5 | .015 | 5 |

s = standard deviation

d.f. = degrees of freedom

* Significantly higher at the .05 confidence level than the other standard deviation estimate for the same pollutant and test gas concentration range.

The cases in which the standard deviations differ significantly for the two agencies but for the same test gas concentration range and pollutant are indicated by an asterisk. The agency-to-agency standard deviations are very consistent in the case of ozone, except for test gas concentration .4 to .5 ppm, in which case only 4 audit points for EPA were included. For $SO_2$, the standard deviation for EPA is higher in all four cases and is significantly higher in two cases. For NO and $NO_x$ the agency-to-agency differences are not as consistent as in the case of $SO_2$, but are not small enough to be disregarded.

There is no apparent difference in equipment used which would explain the agency-to-agency differences in variability. Further investigation to determine whether the observed differences repeat in other experiments and, if so, to determine the cause of the differences would be beneficial.

Table 2-2 presents a "pooled," or combined, standard deviation estimate for each pollutant and test gas concentration range. The pooled standard deviation $s_p$ is defined as follows:

$$s_p = \sqrt{\frac{(N_1-1)s_1^2 + (N_2-1)s_2^2}{N_1 + N_2 - 2}}$$

where

$s_i$, $i = 1, 2$, are the standard deviations for the two agencies, and

$N_i$, $i = 1, 2$, are the numbers of points used in computing $s_1$ and $s_2$, respectively.

## TABLE 2-2

## POOLED STANDARD DEVIATIONS (PPM)

| Test Gas Concentration | Ozone | | $SO_2$ | | NO | | $NO_x$ | |
|---|---|---|---|---|---|---|---|---|
| | $s_p$ | d.f. | $s_p$ | d.f. | $s_p$ | d.f. | $s_p$ | d.f. |
| .4-.5 | .040 | 35 | .051* | 8 | .041 | 8 | .046 | 6 |
| .3-.4 | .040 | 30 | .067 | 47 | .051 | 35 | .047 | 31 |
| .2-.3 | .032 | 66 | .049 | 36 | .041 | 33 | .019 | 24 |
| .1-.2 | .018 | 44 | .028 | 64 | .022 | 91 | .017 | 76 |
| 0-.1 | .014* | 12 | .007 | 10 | .015 | 12 | .018 | 11 |

$s_p$ = pooled standard deviation

d.f. = degrees of freedom

* Computed from EPA data only.

The quantity $s_p$ is said to have $N_1 + N_2 - 2$ degrees of freedom.

Due to the high degree of consistency between the standard deviations for the two agencies for ozone, the pooled standard deviations for this pollutant can reasonably be assumed to characterize the audit uncertainties regardless of the auditing agency. These pooled standard deviations were used to derive a decision rule, presented in Table 2-3, for testing the consistency of an audit point with the machine response. The objective is to determine whether (1) the observed discrepancy can be explained by random variation or (2) the discrepancy is too large to be explained in these terms and, thus, probably indicates a malfunction or severe drift.

Each column in the table corresponding to a particular value of $\alpha$ actually defines a separate decision rule. Suppose, for example, that one adopts the rule in which $\alpha = .2$. Then if the measuring and auditing equipment were both operating properly, 20% of the audit points would be judged inconsistent with the corresponding machine responses due to larger-than-average random errors. The probability of <u>this type</u> of decision error can be reduced by choosing a smaller value of $\alpha$; however, as the probability of this error decreases, the probability (which cannot be computed) of concluding that consistency exists when there is a malfunction or severe drift increases. It is suggested that the $\alpha = .2$ or $\alpha = .1$ decision rules are reasonable compromises, considering the two opposing types of errors, neither of which can feasibly be eliminated absolutely.

In deriving the decision rule, the errors were assumed to be normally distributed; as is mentioned above, the normal hypothesis is discussed in Appendix A.

## TABLE 2-3

## DECISION RULE FOR TESTING CONSISTENCY BETWEEN AUDIT POINT AND MACHINE RESPONSE (OZONE)

| TEST GAS CONCENTRATION (PPM) | REJECT HYPOTHESIS THAT CONSISTENCY EXISTS IF DISCREPANCY* EXCEEDS | | | |
|---|---|---|---|---|
| | $\alpha = .20$ | $\alpha = .10$ | $\alpha = .05$ | $\alpha = .01$ |
| .4 - .5 | .052 (12%) | .068 (15%) | .081 (18%) | .109 (24%) |
| .3 - .4 | .052 (15%) | .068 (19%) | .082 (23%) | .110 (31%) |
| .2 - .3 | .041 (16%) | .053 (21%) | .064 (26%) | .085 (34%) |
| .1 - .2 | .023 (15%) | .030 (20%) | .036 (24%) | .048 (32%) |
| 0 - .1 | .019 (38%) | .025 (50%) | .031 (62%) | .043 (86%) |

$\alpha$ = Probability of erroneously concluding that an inconsistency exists when, in fact, only a much larger than average random error has been observed.

* The "discrepancy" is the absolute value of the instrument response minus the audit test gas concentration, both in ppm.

The percentages given are relative to the test gas concentration mid-range value.

After discussions among the Radian staff and with EPA contact representatives, it was decided not to derive formal decision rules for the other pollutants at this time. The reason is the apparent agency-to-agency differences in the magnitude of the random errors, which is discussed above in connection with Table 2-1. It is somewhat questionable to derive a single decision rule for both agencies in view of these differences, and until or unless the differences are shown to be repeatable under other circumstances, deriving separate decision rules is considered undesirable.

In any case, Table 2-1 and Table 2-2 present all of the necessary information for deriving separate or joint decision rules, respectively. Table 2-3 was derived directly from Table 2-2. The statistical calculations are very simple numerically and involve a straightforward application of the t-statistic, which is discussed in almost every elementary statistics textbook, such as Ref. 2.

## Investigation of Systematic Discrepancies

Tables 2-4 through 2-7 present an analysis of possible systematic discrepancies between audit values and test gas concentrations for different pollutants, test gas concentration ranges, and auditing agencies. A positive value of the mean, $\bar{x}$, indicates that the instrument response was larger on the average than the test gas concentration.

Even if there were no <u>systematic</u> discrepancy, one would not expect the mean $\bar{x}$ to be exactly zero. The question, then, is how large should $\bar{x}$ be in magnitude to arouse suspicion that a systematic, or statistically significant, discrepancy exists?

In the case of ozone, the test gas concentration is larger than the machine response on the average in all but one case presented in Table 2-4, and the differences are statistically significant in all but one case; "statistical significant" is discussed below.

In addition to the statistical significance of the means, however, their magnitudes should also be considered. It is possible for an effect to be repeatable but small in magnitude, or in practical importance. The mean values shown in Table 2-4 indicate that the means are less than 10% of the test gas concentration midrange except for two cases, the one discussed above for which there are only four data points and for the lowest test gas concentration range, for which relative errors were known to be larger than average.

The rightmost columns of Tables 2-4 through 2-7 indicate the cases in which a measurable, or statistically significant, deviation from zero exists. Consider, for example, the first row in Table 2-4. The value .01 in the rightmost column indicates the <u>significance</u> of the value of $\bar{x}$: Given the number of data points available (4) and random variation observed (the standard deviation is .018) in this case, the probability is only .01 that the mean would differ from 0 in absolute value by as much as .052, the magnitude of $\bar{x}$, <u>if there were no systematic difference</u>. Thus, since this probability is very low, there is evidence that a systematic discrepancy exists in this case. Thus, $\bar{x}$ is said to differ from 0 to a statistically significant extent at the .01 confidence level.

For $SO_2$ (Table 2-5), there is no clear indication of a systematic error. For NO and $NO_x$, the machine response is generally larger than the test gas concentration, but this effect is again less than 10% in most cases.

TABLE 2-4

STATISTICS ON RANDOM ERRORS* IN OZONE AUDIT POINTS: ALL INSTRUMENTS, ALL DATES, CONCENTRATIONS IN PPM.

| Test Gas Concentration | Agency | $\bar{x}$ | s | N | t | Significant at the $\alpha$ - level |
|---|---|---|---|---|---|---|
| .4-.5 | EPA | -.052 | .018 | 4 | -5.945 | .01 |
| .4-.5 | Radian | -.021 | .041 | 33 | -2.995 | .01 |
| .3-.4 | EPA | -.025 | .041 | 16 | -2.401 | .05 |
| .3-.4 | Radian | .026 | .039 | 16 | 2.612 | .025 |
| .2-.3 | EPA | -.017 | .034 | 32 | -2.864 | .01 |
| .2-.3 | Radian | -.004 | .030 | 36 | -0.871 | - |
| .1-.2 | EPA | -.011 | .018 | 34 | -3.553 | .005 |
| .1-.2 | Radian | -.014 | .017 | 12 | -3.009 | .025 |
| 0-.1 | EPA | -.007 | .014 | 13 | -1.829 | .1 |

$\bar{x}$ = mean of instrument response minus test gas concentration

s = standard deviation of this difference

N = number of data points used

$t = \frac{\bar{x}}{s/\sqrt{N}}$, used to test the statistical significance of the deviation of $\bar{x}$ from 0.

* Analysis of instrument value minus test gas concentration.

TABLE 2-5

STATISTICS ON RANDOM ERRORS IN $SO_2$ AUDIT POINTS:

ALL INSTRUMENTS, ALL DATES, CONCENTRATIONS IN PPM

| Test Gas Concentration | Agency | $\bar{x}$ | s | N | t | Significant at the $\alpha$ - level |
|---|---|---|---|---|---|---|
| .4-.5 | EPA | -.0190 | .0508 | 9 | -1.122 | - |
| .4-.5 | Radian | -.0360 | - | 1 | - | - |
| .3-.4 | EPA | -.0031 | .0772 | 23 | - .192 | - |
| .3-.4 | Radian | .0078 | .0568 | 26 | .705 | - |
| .2-.3 | EPA | .0056 | .0577 | 22 | .454 | - |
| .2-.3 | Radian | .0151 | .0340 | 16 | 1.781 | .1 |
| .1-.2 | EPA | -.0070 | .0329 | 31 | -1.180 | - |
| .1-.2 | Radian | .0017 | .0236 | 35 | .416 | - |
| 0-.1 | EPA | .0020 | .0170 | 2 | .167 | - |
| 0-.1 | Radian | -.0017 | .0051 | 10 | -1.045 | - |

TABLE 2-6

STATISTICS ON RANDOM ERRORS IN NO AUDIT POINTS:
ALL INSTRUMENTS, ALL DATES, CONCENTRATIONS IN PPM

| Test Gas Concentration | Agency | $\bar{x}$ | s | N | t | Significant at the α - level |
|---|---|---|---|---|---|---|
| .4-.5 | EPA | .0228 | .0354 | 6 | 1.58 | .2 |
| .4-.5 | Radian | -.0505 | .0487 | 4 | 2.07 | .2 |
| .3-.4 | EPA | .0507 | .0437 | 14 | 4.34 | .001 |
| .3-.4 | Radian | .0170 | .0551 | 23 | 1.48 | .2 |
| .2-.3 | EPA | .0450 | .0457 | 27 | 5.12 | .001 |
| .2-.3 | Radian | -.0021 | .0168 | 8 | - .36 | - |
| .1-.2 | EPA | .0205 | .0249 | 44 | 5.45 | .001 |
| .1-.2 | Radian | .0045 | .0193 | 49 | 1.63 | .2 |
| 0-.1 | EPA | .0093 | .0187 | 8 | 1.40 | - |
| 0-.1 | Radian | -.0030 | .0081 | 6 | - .90 | - |

TABLE 2-7

STATISTICS ON RANDOM ERRORS IN $NO_x$ AUDIT POINTS: ALL INSTRUMENTS, ALL DATES, CONCENTRATIONS IN PPM

| Test Gas Concentration | Agency | $\bar{x}$ | s | N | t | Significant at the $\alpha$ - level |
|---|---|---|---|---|---|---|
| .4-.5 | EPA | .0200 | .0282 | 4 | 1.42 | - |
| .4-.5 | Radian | -.0425 | .0590 | 4 | -1.44 | - |
| .3-.4 | EPA | .0425 | .0246 | 12 | 5.98 | .001 |
| .3-.4 | Radian | .0191 | .0556 | 21 | 1.57 | .2 |
| .2-.3 | EPA | .0184 | .0180 | 18 | 4.33 | .001 |
| .2-.3 | Radian | -.0029 | .0216 | 8 | - .38 | - |
| .1-.2 | EPA | .0086 | .0140 | 31 | 3.40 | .005 |
| .1-.2 | Radian | .0057 | .0186 | 47 | 2.09 | [illegible] |
| 0-.1 | EPA | .0001 | .0195 | 7 | .02 | - |
| 0-.1 | Radian | .0043 | .0150 | 6 | .71 | - |

## 3.0 ANALYSIS OF ZERO-SPAN DATA

In this section, an analysis is made of the relationship between the test gas concentrations used in the daily zero-span autocalibrations and the corresponding machine responses. Since these responses are recorded relative to the most recent multi-point calibration, not relative to the daily autocalibrations, their scale is constant between multi-point calibratons. Thus, it is possible to examine the responses to see if there is a drift or change in the amount of random scatter as the time since the last multi-point increases.

Certain adjustments, including a check on the purity of the zero gas and a recalibration of the span gas concentration, are performed during a multi-point. This provides a physical reason for analyzing trends relative to the recalibration point.

The purpose of this chapter is to quantify the zero-span errors. This analysis is useful (1) in evaluating the accuracy of the zero-span autocalibrations and (2) in a quantitative sense, in assessing the usefulness of the zero-span data as indicators of the need for a multi-point calibration or a quality-assurance audit; only malfunctions which induce errors significantly larger than normally expected random variation can be perceived by monitoring the zero-span data.

Regarding point (2) above, it was observed that the great majority of the zero-span data either fell within the normal range of variation, as depicted by the figures in this chapter, or were clearly disjoint from most of the points. The data in the latter class generally were observed either just before system downtime or immediately after the system had resumed

operation after a period of known malfunction. Thus, the strong indication is that the zero-span data are useful in indicating an abnormal condition.

Typical indications of malfunctions observed are a response of less than 10 ppb to a span gas with concentration of over 300 ppb and a response of over 50 ppb to the zero gas.

The data are shown graphically in Figures 3-1 - 3-12. Means and standard deviations of test gas concentration-machine sensor response are presented. These statistics were computed for successive four-day periods throughout the month of September, 1976, and are plotted versus the beginning of the four-day period. These data are presented in tabular form in Appendix C.

The month of September actually extends over parts of two multi-point calibration periods, with recalibrations being performed near the middle of the month. Thus, the general similarity of the left and right sides of the plots is an indication of the consistency of the random variations from period to period. The calibration dates for all trailers are given in Appendix C.

Plots are presented for ozone, $SO_2$, and $NO_x$. The values for NO were very similar to those for $NO_x$, but the means and standard deviations were slightly smaller in magnitude (by about 10%) for NO than for $NO_x$. The day-to-day agreement for the NO and $NO_x$ values was very close. For this reason, it was felt that the plots for $NO_x$, along with the comments above, adequately represented the zero-span data for both pollutants.

The following general observations can be made:

(1) There is no evidence of any long-term, systematic increase in the magnitudes of the test gas concentration-machine response differences with time.

(2) The day-to-day variability does not appear to increase with time since the last multi-point calibration. This was concluded because there is no increasing trend in the standard deviations with time.

(3) The trailer-to-trailer differences appear to be very random; that is, there is no evidence that some trailers exhibit greater tendencies toward drift or day-to-day fluctuations than others.

(4) The vast majority of the four-day mean values of the response to zero gas fall within an interval of width 15 ppb for each gas. The $NO_x$ response tends to be positive by a few (about 5) ppb on the average.

(5) The vast majority of the four-day mean values of the span gas concentration minus the machine response fall within an interval of width 80 ppb for each gas. The $NO_x$ span gas concentration is larger than the machine response by about 10 ppb on the average.

(6) The four-day standard deviations of the zero-gas responses are generally less than about 7, 3, and 10 ppb for ozone, $SO_2$, and $NO_x$, respectively.

(7) The four-day standard deviations of the span gas concentration minus the machine sensor response are generally less than 20 ppb for all gases.

FIGURE 3-1

FOUR DAY MEAN VALUE OF MACHINE $O_3$ SENSOR RESPONSE TO ZERO GAS VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

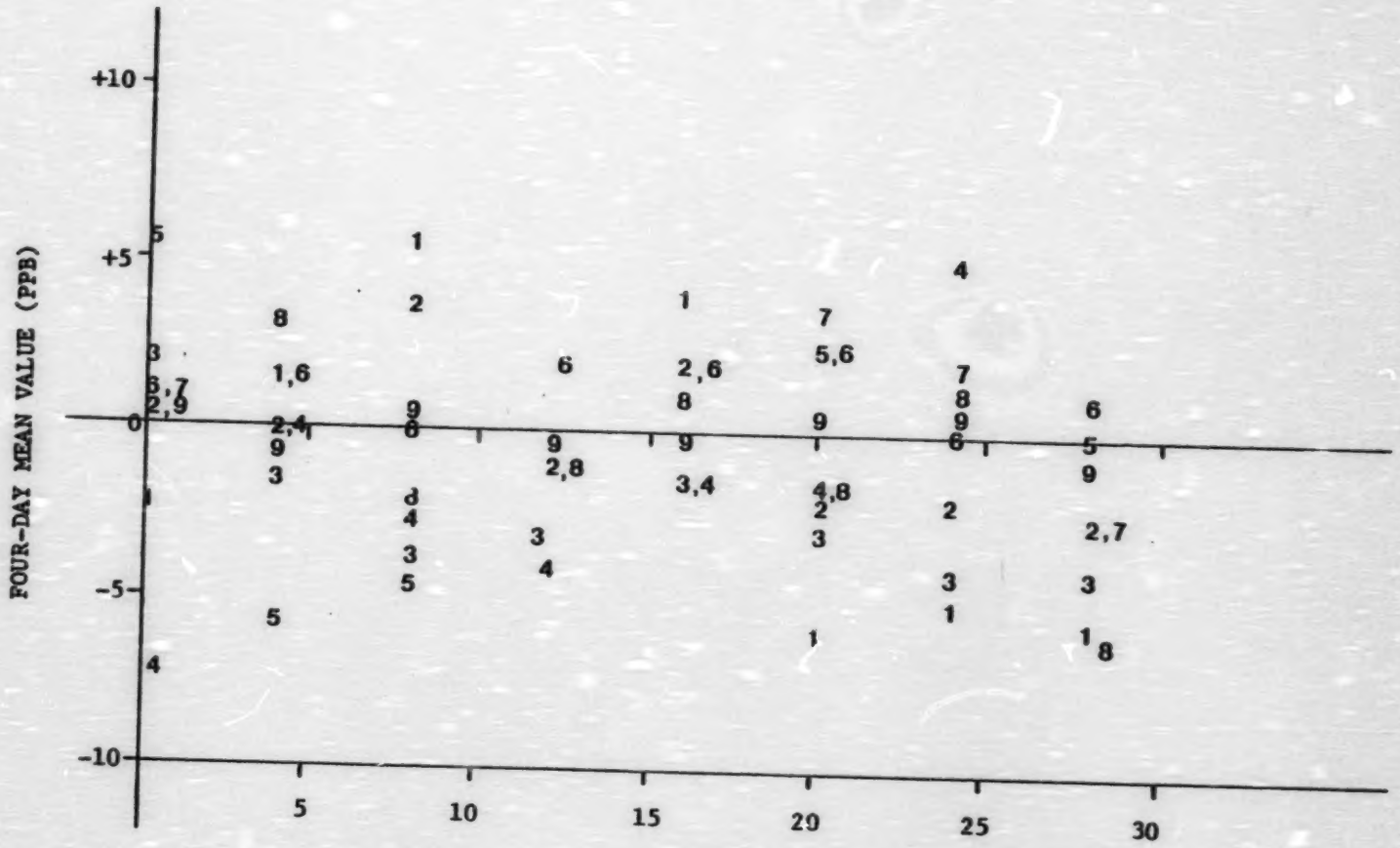


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FIGURE 3-2

FOUR-DAY STANDARD DEVIATION OF MACHINE $O_3$ SENSOR RESPONSE TO ZERO GAS VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

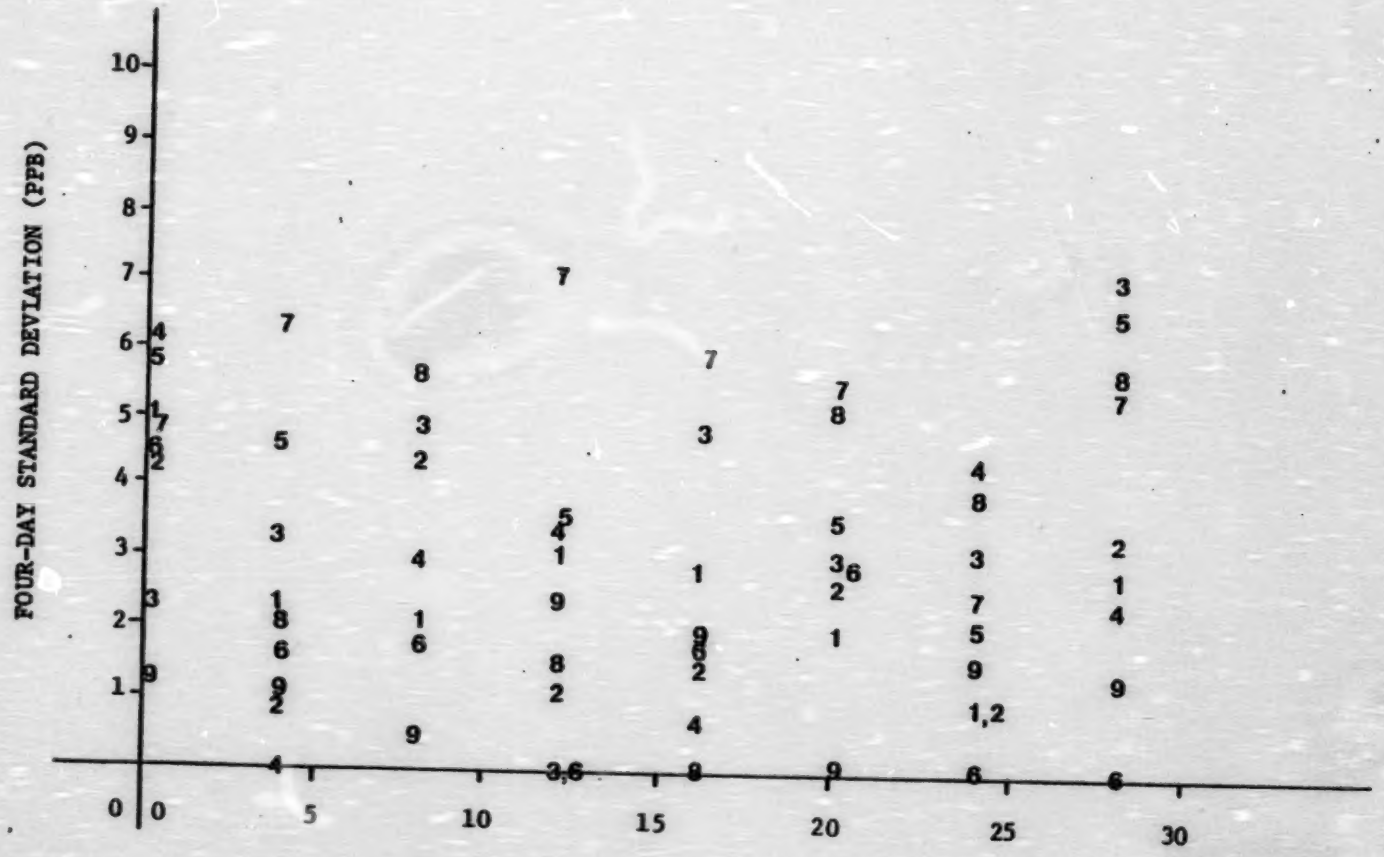


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FIGURE 3-3

FOUR-DAY MEAN VALUE OF SPAN GAS CONCENTRATION MINUS
MACHINE $O_3$ SENSOR RESPONSE VERSUS TIME
SINCE LAST MULTI-POINT CALIBRATION

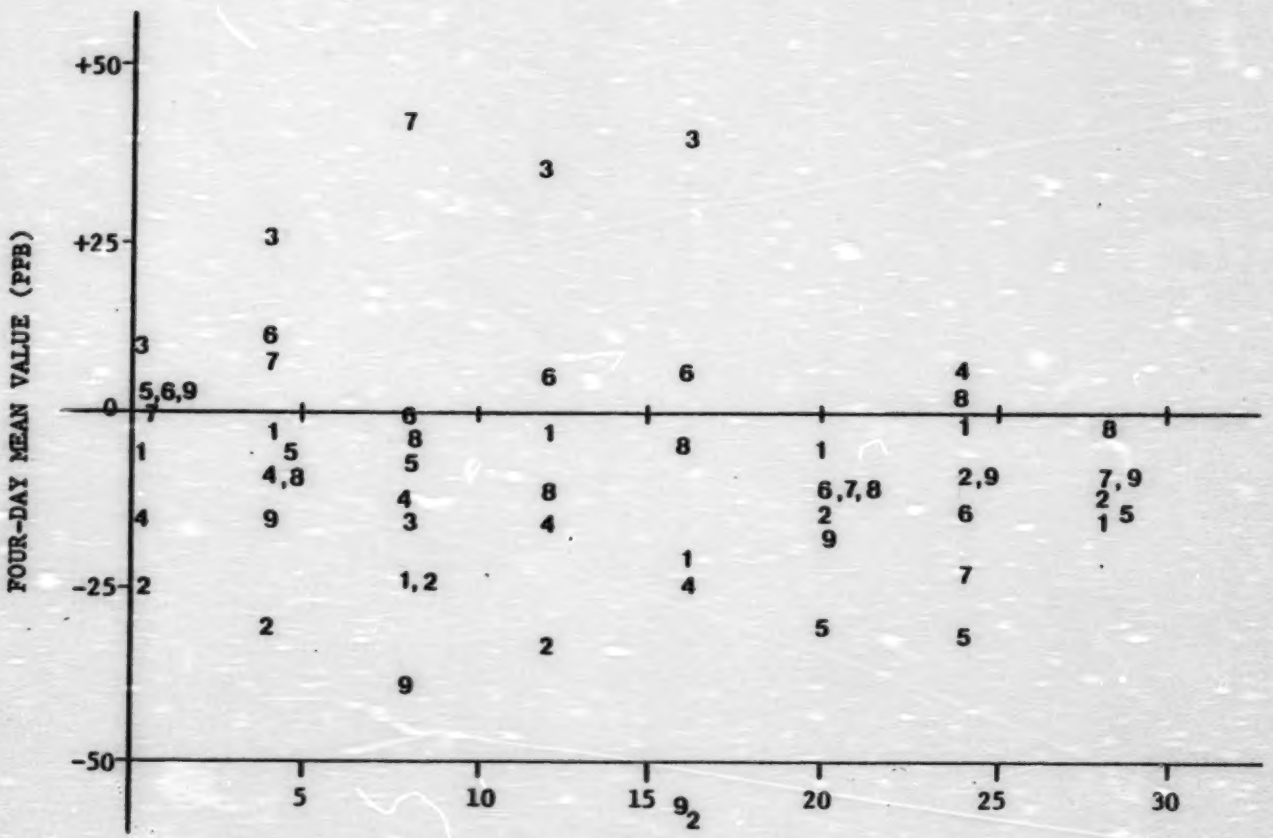


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FIGURE 3-4

FOUR-DAY STANDARD DEVIATION OF SPAN GAS CONCENTRATION
MINUS MACHINE $O_3$ SENSOR RESPONSE VERSUS
TIME SINCE LAST MULTI-POINT CALIBRATION

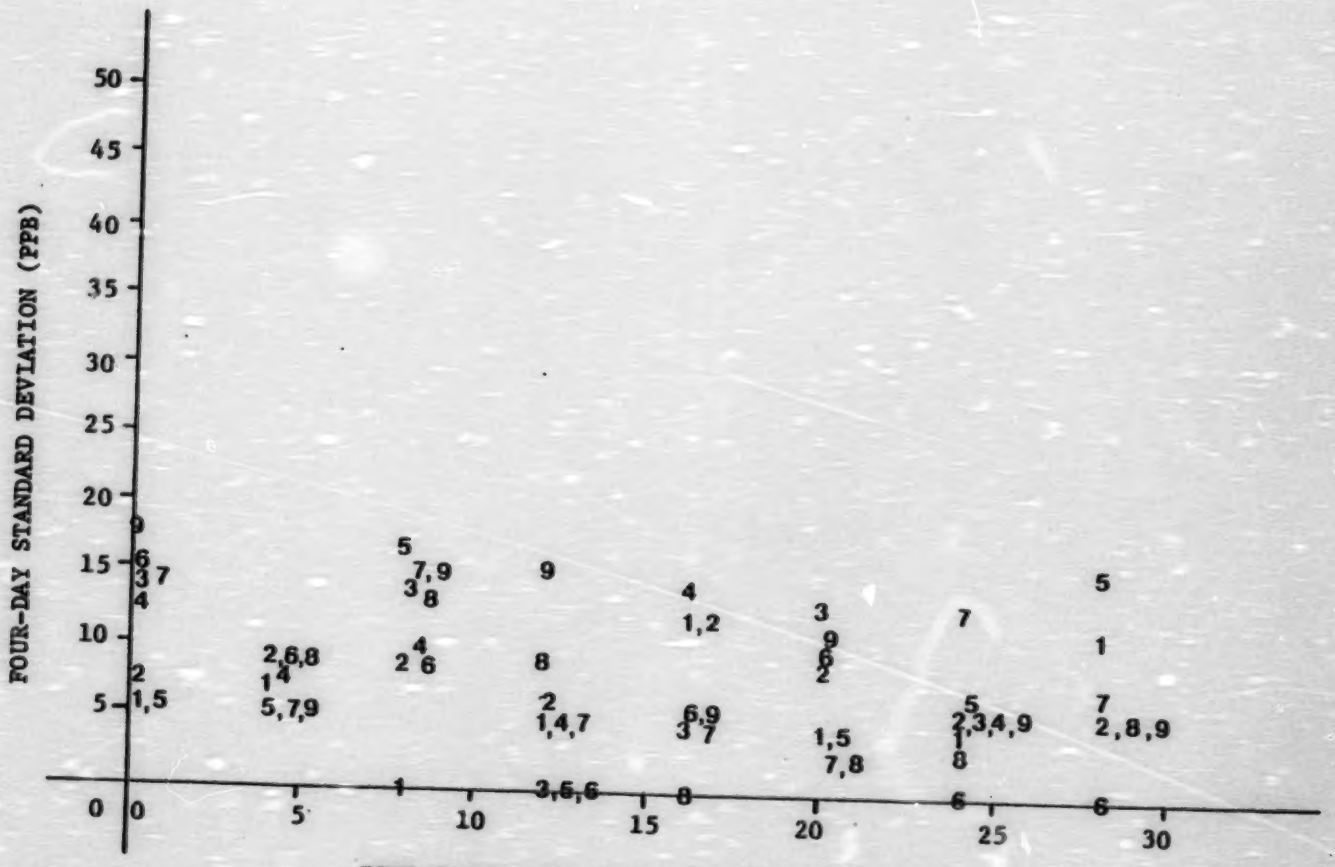


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FIGURE 3-5

FOUR-DAY MEAN VALUE OF MACHINE $SO_2$ SENSOR RESPONSE
TO ZERO GAS VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

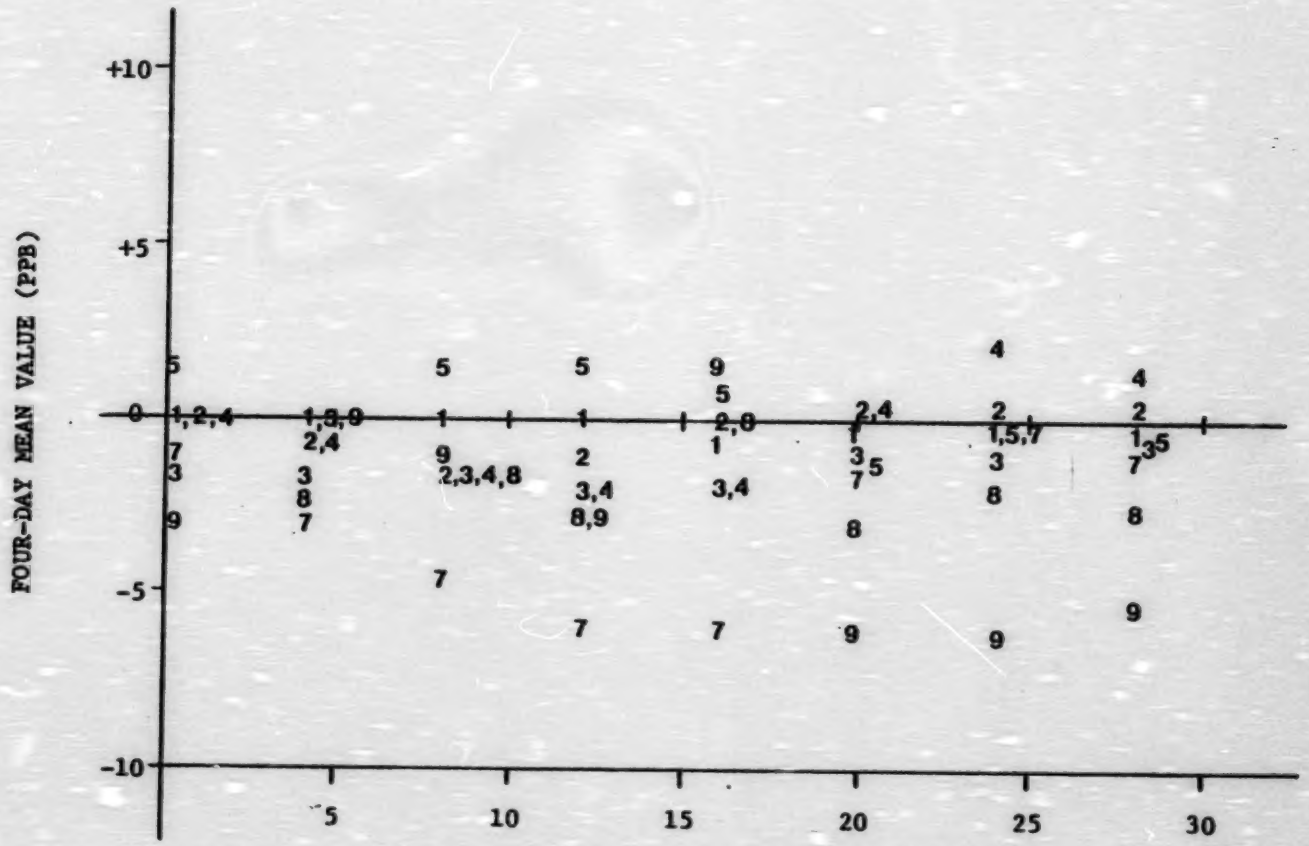


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FIGURE 3-6

FOUR-DAY STANDARD DEVIATION OF MACHINE $SO_2$ SENSOR
RESPONSE TO ZERO GAS VERSUS TIME
SINCE LAST MULTI-POINT CALIBRATION

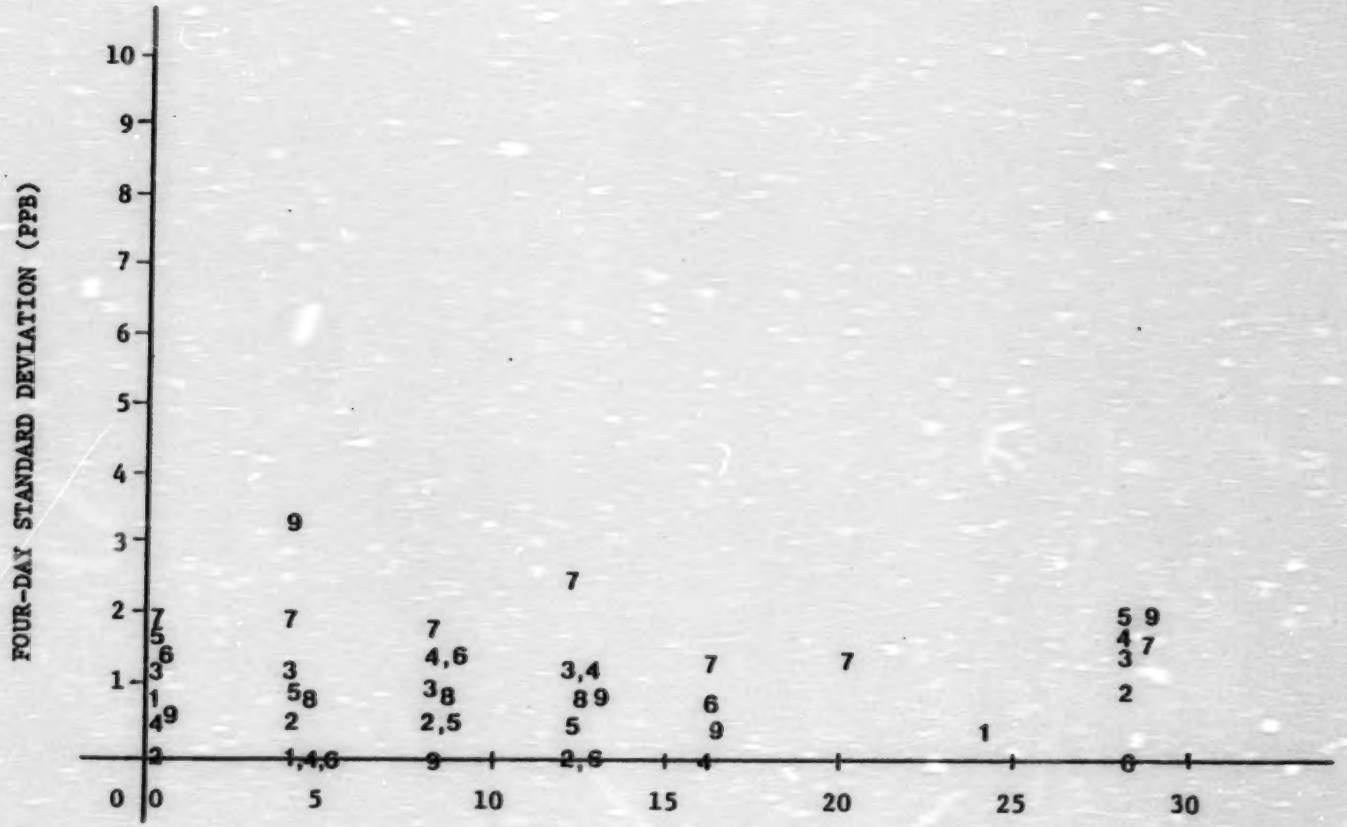


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FIGURE 3-7

FOUR-DAY MEAN VALUE OF SPAN GAS CONCENTRATION
MINUS MACHINE $SO_2$ SENSOR RESPONSE VERSUS
TIME SINCE LAST MULTI-POINT CALIBRATION

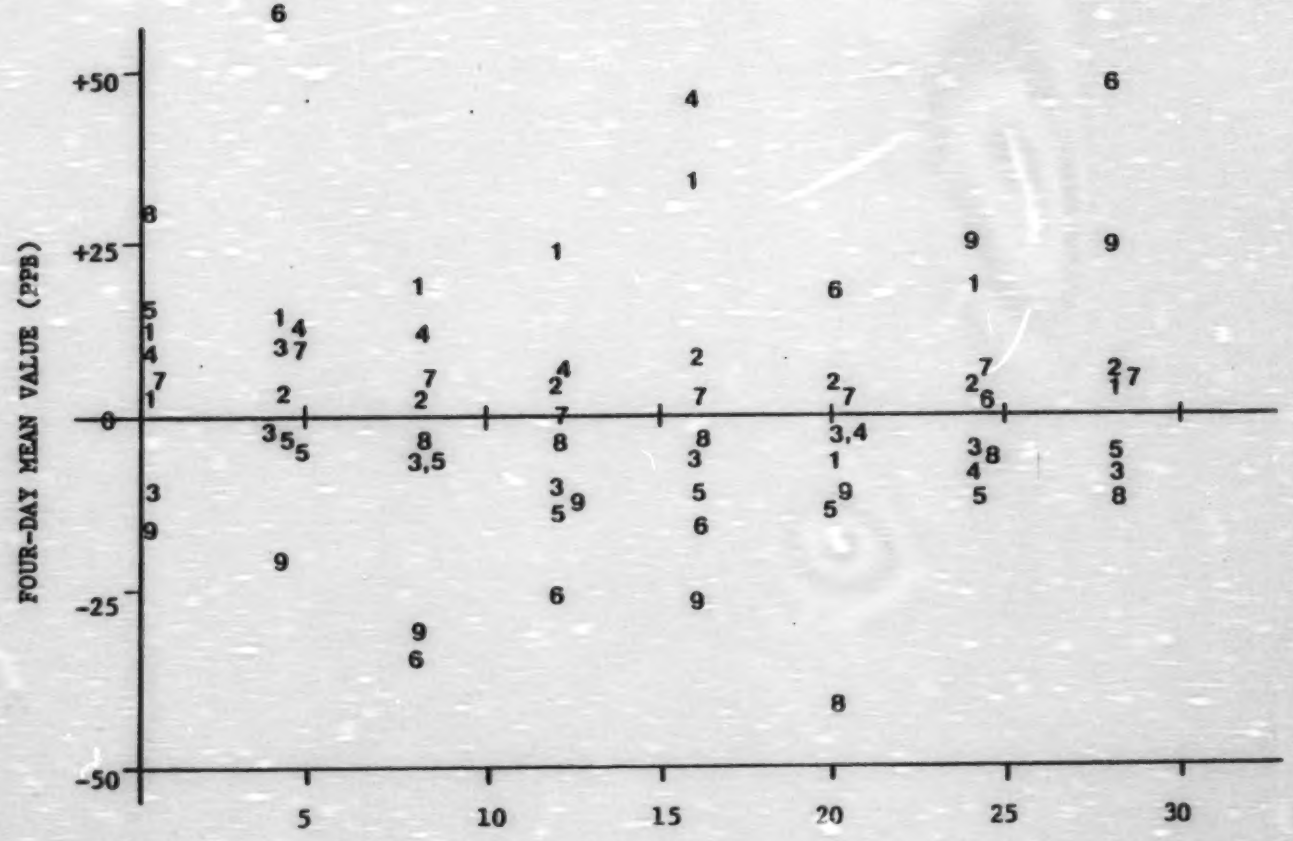


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FIGURE 3-8

FOUR-DAY STANDARD DEVIATION OF SPAN GAS CONCENTRATION
MINUS MACHINE $SO_2$ SENSOR RESPONSE VERSUS
TIME SINCE LAST MULTI-POINT CALIBRATION

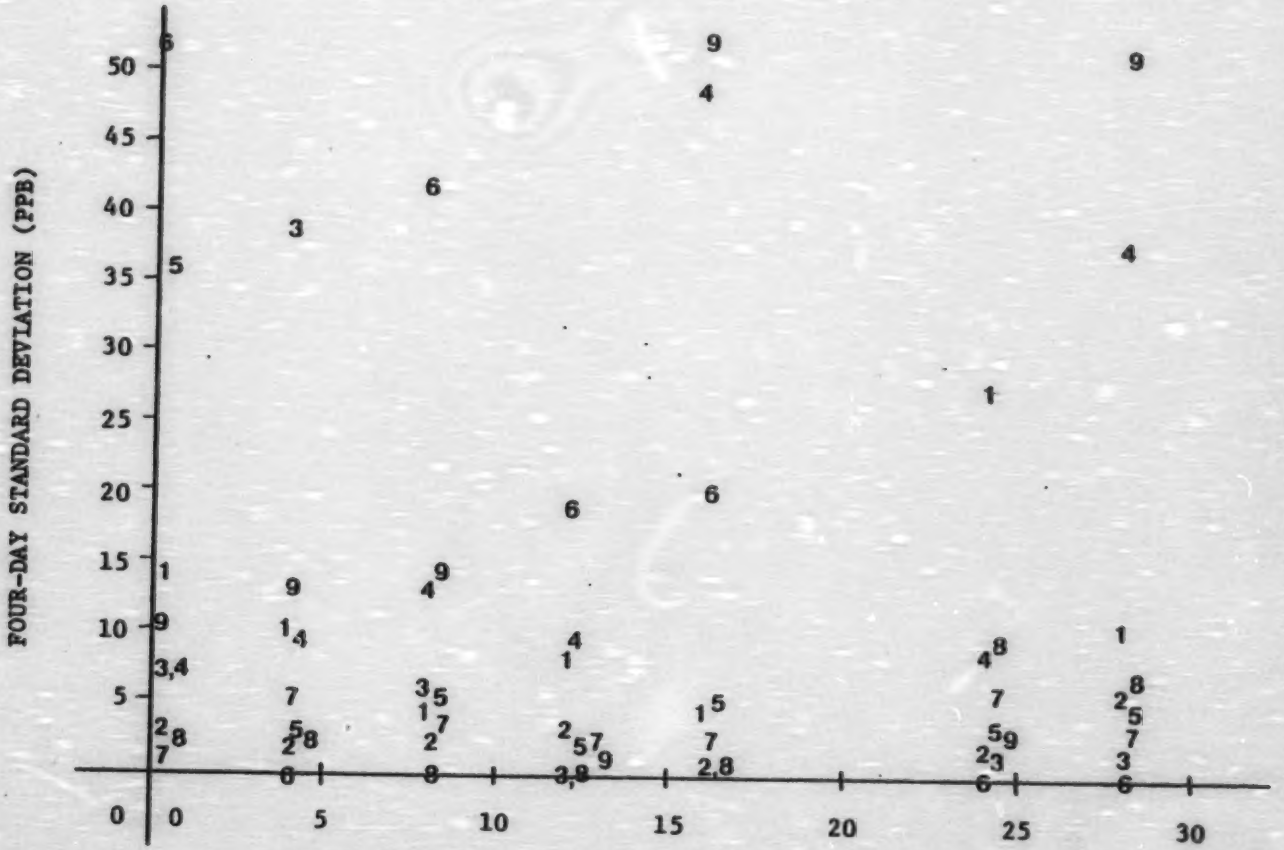


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FIGURE 3-9

FOUR-DAY MEAN VALUE OF MACHINE $NO_x$ SENSOR RESPONSE TO ZERO GAS VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

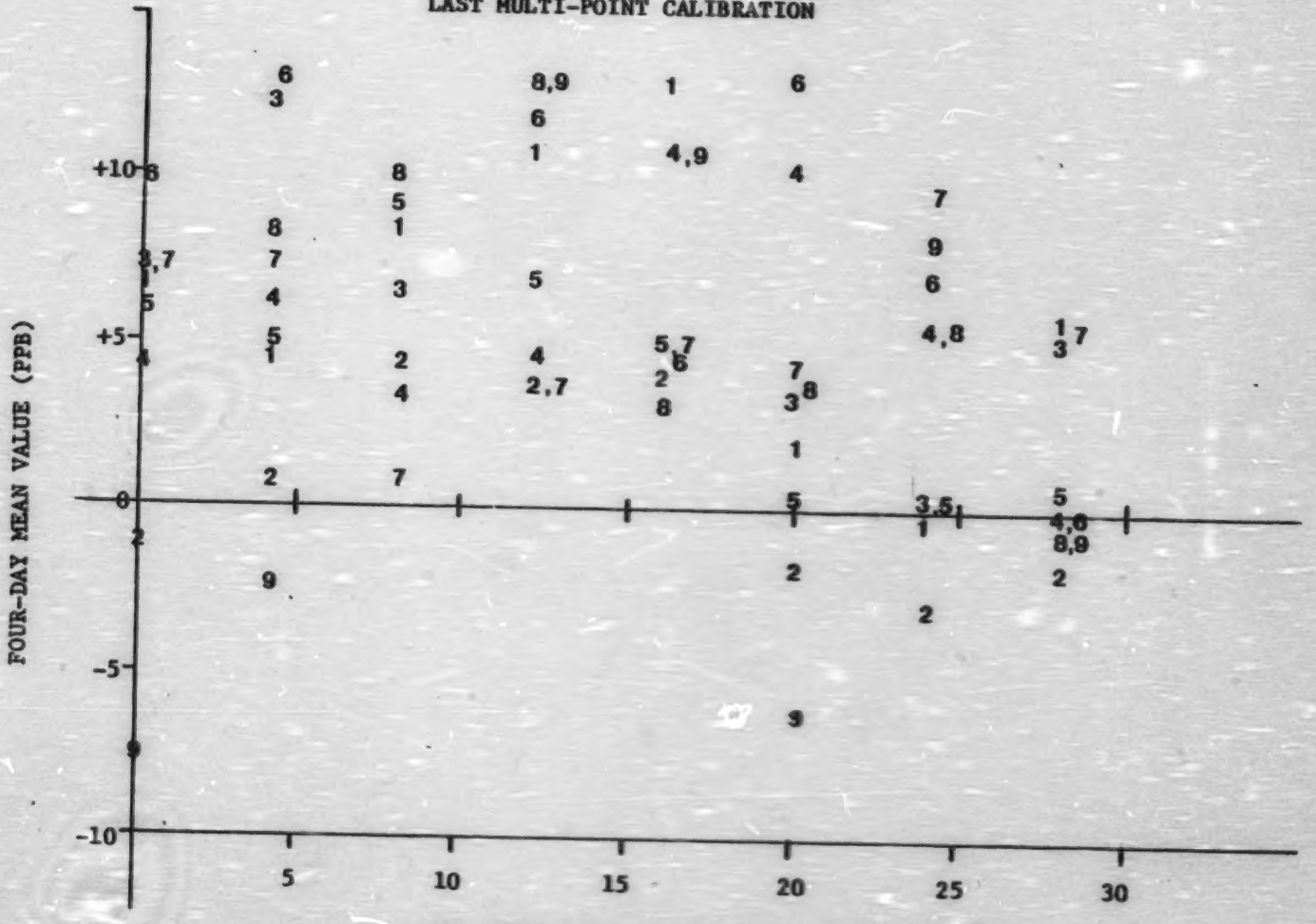


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FIGURE 3-10

FOUR-DAY STANDARD DEVIATION OF MACHINE NO$_x$ SENSOR RESPONSE TO ZERO GAS VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

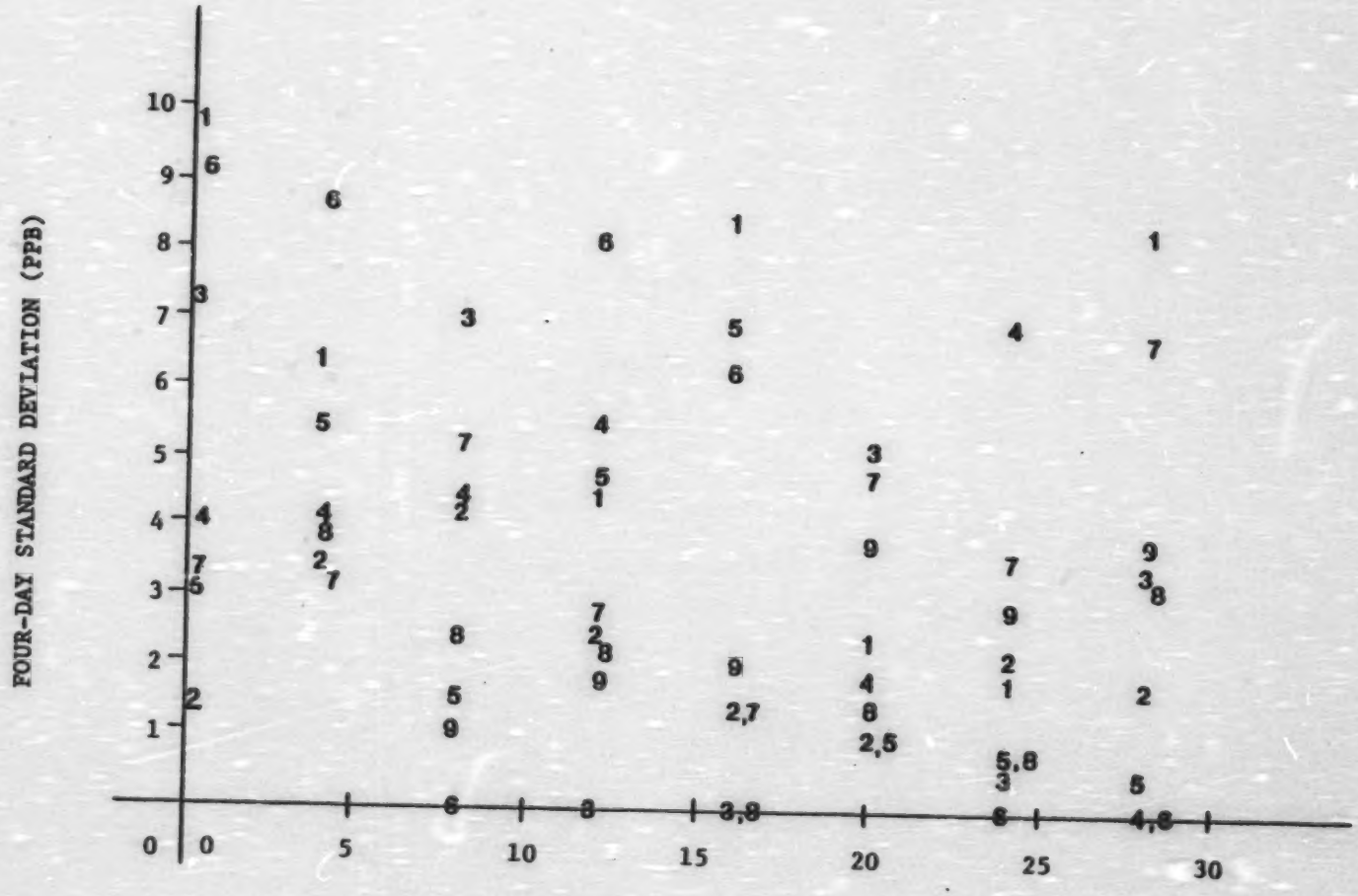


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FIGURE 3-11

FOUR-DAY MEAN VALUE OF SPAN GAS CONCENTRATION MINUS MACHINE $NO_x$ SENSOR RESPONSE VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

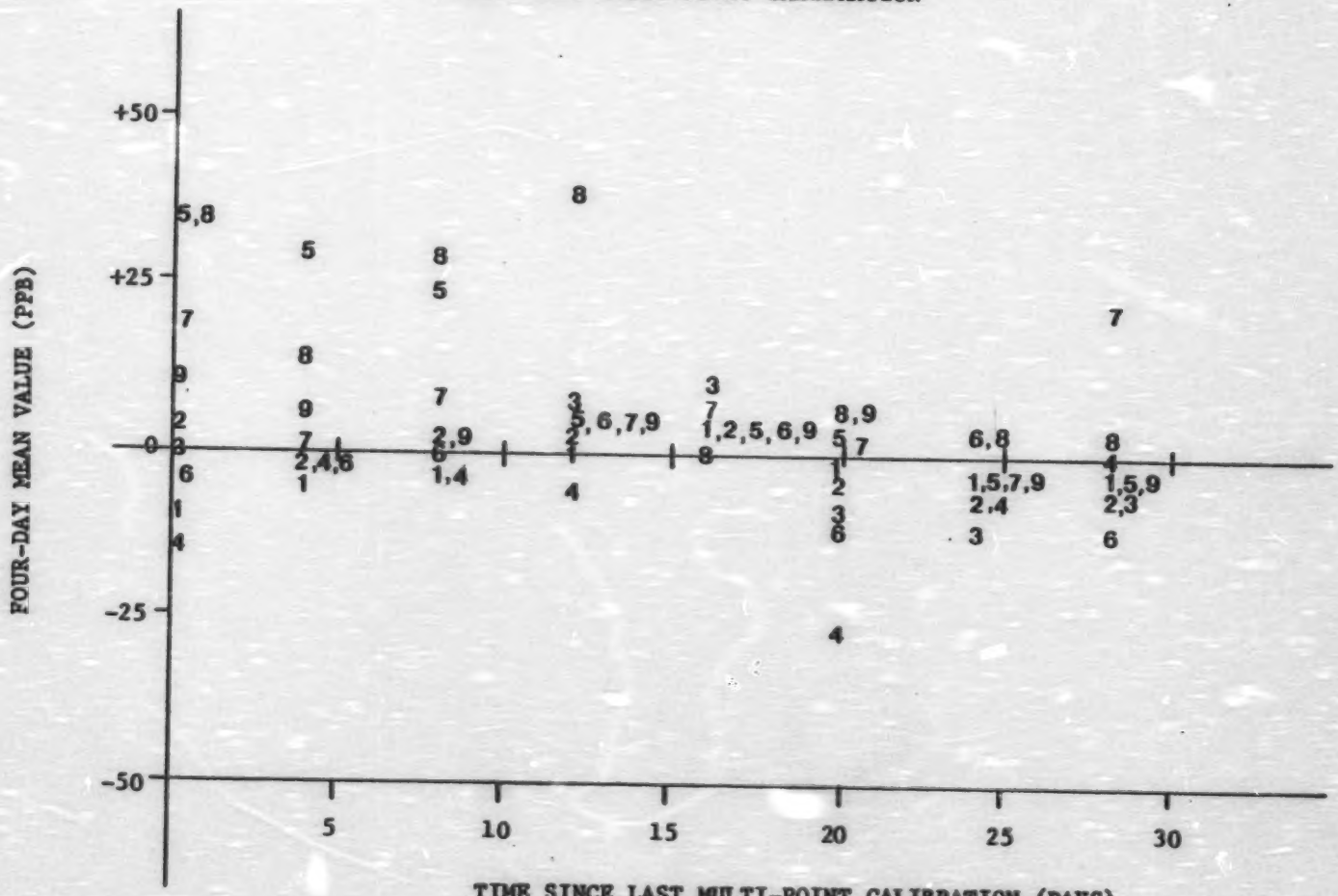


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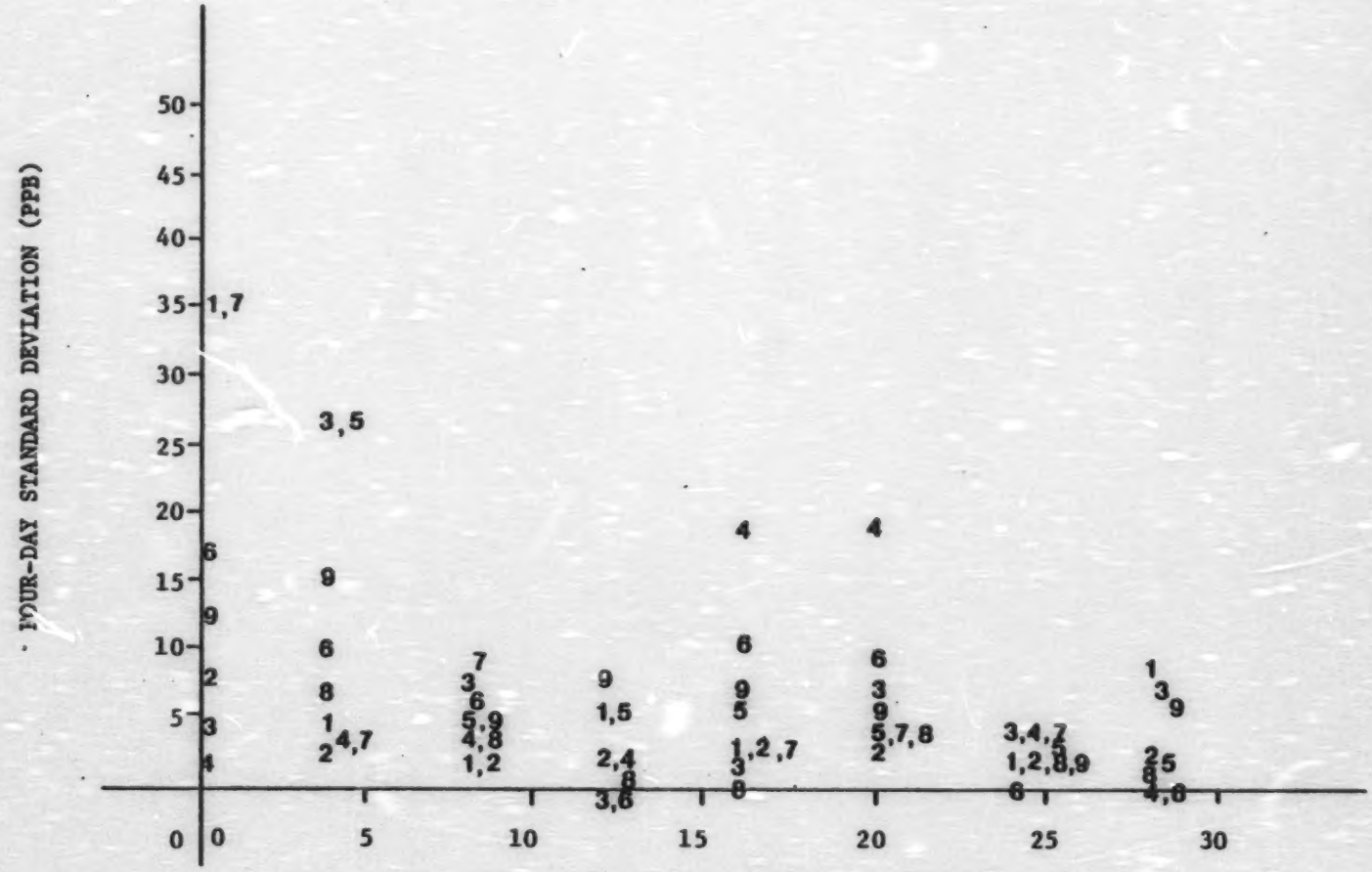
FIGURE 3-12

FOUR-DAY STANDARD DEVIATION OF SPAN GAS CONCENTRATION
MINUS MACHINE $NO_x$ SENSOR RESPONSE VERSUS TIME
SINCE LAST MULTI-POINT CALIBRATION

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## 4.0 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

In this report, an analysis is presented of the errors involved in measurements made with Radian-built air-monitoring trailers. Measurements of the concentrations of ozone, $SO_2$, NO, and $NO_x$ were compared to corresponding "known" test gas samples used in quality assurance audits and daily zero-span autocalibrations to quantify the errors.

The error analysis presented here was motivated primarily by the need for (1) empirically based guidelines for deciding whether an audit test gas concentration and the corresponding machine response are consistent within normally expected random variation and (2) an assessment of the usefulness of zero-span data in validating the air quality measurements on a day-to-day basis and for recognizing the need for an audit or recalibration.

The major work objective involved in resolving these concerns is quantifying the errors expected when the equipment has no malfunction. The errors in the audit process are discussed in Section 2.0, and the errors in the zero-span autocalibrations are discussed in Section 3.0. The primary measure of random variation employed here is the standard deviation. An error which is normally distributed (see Appendix A) falls within plus and minus one standard deviation of its mean value about 68% of the time; thus, the standard deviation has an easily understood meaning.

A formal decision rule for testing the consistency of an ozone audit result is presented in Table 2-3. This table presents maximum discrepancies between the test gas concentration and the machine response which can reasonably be

expected if the equipment has no malfunction. For a ozone test gas concentration of 100 to 500 ppb, the random errors are shown to be less than about 15% in 80% of the cases and less than about 20% in 90% of the cases.

Differences in random variability between EPA and Radian audits were observed for the other pollutants investigated. It is felt that these discrepancies should be either verified and explained or shown to be anomalies of this particular experiment before formal decision rules are established. The standard deviations, from which such a rule would directly follow, are presented for all cases, however, in Table 2-1 and 2-2.

The variability of the zero-span data are also quantified. No systematic long-term drift is observed, and there is no evidence of a trailer-dependent bias. The standard deviations were computed separately for successive four-day periods since the last multipoint calibration, for different pollutants, and for zero as opposed to span gas. The standard deviation in the majority of cases during proper machine operation are shown to be less than 10 ppb for the zero gas and less than 20 ppb for the span gas. The results are presented in detail in Figures 3-1 through 3-12.

When the results fell outside these ranges, the errors were usually extreme, e.g., a response of over 50 ppb to the zero gas or less than 30 ppb to a span gas of concentration over 300 ppb. These conditions usually occurred just before or immediately following a period of system downtime. Thus, the demarcation between normally varying and erroneous zero-span results was usually very clear and explainable in terms of system malfunction status.

In addition to random variability, the tendency of the machine response to be measurably lower or higher than the test

gas concentration was analyzed. This effect was observed in some cases but the average discrepancy was usually less than and never extreme compared to the point-to-point standard deviation. In the ozone audits, for example, the test gas concentration was genrally greater than the machine response by somewhat less than 10%. It will be beneficial to observe whether the consistent differences which were observed repeat in subsequent data collections.

The audit data used in this study, while rather extensive, were not collected specifically for an error analysis. The imbalance in the numbers of points for different test gas concentrations, for different pollutants, and for different auditing agencies (EPA or Radian) imposed particularly stringent limitations on the analysis. The number of points in each such "cell" or classification varies from 0 to 49. In the cases where there are only a few data points, the results cannot be viewed as final.

It would be of value, moreover, to ascertain whether the observed differences in random variability between auditing agencies is an anomaly associated with this particular data set or a real effect. One such observation was that EPA's auditing variability was greater than Radian's for every test gas concentration range observed for $SO_2$.

Furthermore, only a tentative resolution of the type of random distribution was possible, due to the small numbers of data available for some classifications. The normal distribution, however, is shown in Appendix A to fit the data within reasonable bounds.

For the reasons discussed above, it is recommended that a follow-up study of the random measurement errors to verify and extend the results presented here would be beneficial. A proposed experimental design, including a list of physical questions to be resolved, is presented in Appendix B.

## REFERENCES


1. Siegel, Sidney, Nonparametric Statistics, McGraw-Hill Book Company, 1956.

2. Snedecor, George W., and William G. Cochran, Statistical Methods, The Iowa State University Press, Ames, Iowa, 1967.

3. -----, "Interim Report on Air Monitoring at Nine Locations in Southern Louisiana," Radian Corporation, December 23, 1976.

# APPENDIX A
# TESTS OF THE NORMALITY OF THE RANDOM ERRORS

The association of probabilities with magnitudes of errors, as in the development of a decision rule for testing an audit point (Section 2.0), is dependent upon the type of statistical distribution of the random errors. The normal distribution, a well-known distribution which is symmetric about its mean and is sometimes referred to as the "bell-shaped curve," is very commonly found to fit errors and other random effects observed in nature. For this and other reasons, the normal distribution was investigated as an approximation to the error distribution of the air pollution data.

Due to the observed variations of the standard deviations with performing agency and test gas concentration, it was felt that the data must be analyzed on a partitioned basis. The number of data points in one cell, determined by test gas concentration interval, pollutant, and performing agency, is sometimes very small and varies greatly, having a maximum of 49. The test for normality in this case, then, cannot be performed as a single, clearly defined hypothesis test which unambiguously resolves the question.

The complex statistical dependencies which almost certainly exist between data for different test gas concentrations, but for the same performing agency and pollutant, further militate against anything but an heuristic resolution of the normality question. These dependencies are due to the usual performance of audits for several pollutant concentrations on the same day. The concentrations vary from audit to audit, however.

It is felt, however, that the results of this appendix indicate no dramatic or systematic deviation from the normal distribution. Thus, the normal assumption, while definitely is not proved to be strictly valid, is believed to be a reasonable working hypothesis for the purposes of this report.

Of the several tests of the normal hypothesis that can be made, the skewness and kurtosis tests were chosen (Ref. 2).

The skewness coefficient $g_1$ is defined as follows:

$$g_1 = \frac{m_3}{(m_2)^{3/2}}$$

where

$$m_j = \frac{\sum_{i=1}^{N} (x_i - \bar{x})^j}{N},$$

that is, $m_j$ is the $j^{th}$ moment about the mean.

For the normal distribution, the skewness is zero. Non-zero skewness indicates that the distribution is asymmetric. Positive skewness shows that the distribution has a long tail to the r[illegible], that is, that there are fewer points above the mean than below, but that the points above the mean have more extreme values as a whole. If the skewness is negative, there is a long tail to the left.

If a random variable is observed consistently to have positive skewness, a logarithmic transformation frequently yields a normal random variable. The convenience of interpretation of skewness in determining whether a normality-inducing transformation is feasible was one reason for the use of the skewness coefficient.

The kurtosis coefficient $g_2$ is defined here as follows:

$$g_2 = \frac{m_4}{m_2^2} - 3$$

The value of $g_2$ is zero for the normal distribution. A positive kurtosis indicates an excess of points very near the mean and far from the mean, with a decrease in the number of points in between, relative to the normal. A distribution with negative kurtosis has a flatter peak than the normal.

It is evident, then, that the skewness and kurtosis coefficients are very easily interpreted geometrically.

For a sample size of 50, a skewness value greater than .534 in magnitude is statistically significant at the .05 level. The threshold value for a sample size of 25 is .711.

For a sample size of 50, the kurtosis coefficient is statistically significantly different from zero at the .05 level if it is greater than .99 or less than -.85. Critical kurtosis tables for small sample sizes are said not presently to exist in Ref. 2.

There are other tests for normality for which critical values are known for all sample sizes, such as the Kolmogoroff-Smirnoff test (Ref. 1). For small sample sizes, however, the hypothesis test is so insensitive that it has very little meaning in an individual case, anyway.

The skewness and kurtosis coefficients for ozone, $SO_2$, NO, and $NO_x$ are presented in Tables A-1 through A-4, respectively.

For ozone, it is observed that there are four negative and five positive skewness values and five negative and four positive kurtosis values. Furthermore, the positives and negatives have no apparent systematic pattern.

For $SO_2$, the skewness values are mainly positive, although two of nine values are negative, and another is zero to two significant figures. There is some evidence of positive skewness in the middle-range of test gas concentration, but the skewness coefficients even here are statistically significant in only two of six cases. The consistency of the positive signs is possibly related to the test gas concentration interval-to-interval dependencies, mentioned earlier in this appendix.

The $SO_2$ kurtosis coefficients, having six positive and three negative values, have no consistent deviation from zero.

For NO and $NO_x$, the skewness coefficients are small in magnitude and have mixed signs. The kurtosis coefficients also vary randomly about zero.

## TABLE A-1
## SKEWNESS AND KURTOSIS STATISTICS (OZONE)

| Test Gas Concentration | Agency | N | Skewness | Kurtosis |
|---|---|---|---|---|
| .4-.5 | EPA | 4 | .94 | - .83 |
| .4-.5 | Radian | 33 | - .64 | - .57 |
| .3-.4 | EPA | 16 | 1.18 | 1.57 |
| .3-.4 | Radian | 16 | - .33 | -1.21 |
| .2-.3 | EPA | 32 | .41 | .45 |
| .2-.3 | Radian | 36 | 2.39 | 9.75 |
| .1-.2 | EPA | 34 | - .10 | - .69 |
| .1-.2 | Radian | 12 | - .05 | -1.27 |
| 0-.1 | EPA | 13 | 1.07 | .04 |
| 0-.1 | Radian | - | - | - |

## TABLE A-2

## SKEWNESS AND KURTOSIS STATISTICS ($SO_2$)

| Test Gas Concentration | Agency | N | Skewness | Kurtosis |
|---|---|---|---|---|
| .4-.5 | EPA | 9 | - .37 | -1.13 |
| .4-.5 | Radian | 1 | - | - |
| .3-.4 | EPA | 23 | .83 | .99 |
| .3-.4 | Radian | 26 | 1.45 | 2.86 |
| .2-.3 | EPA | 22 | .82 | .66 |
| .2-.3 | Radian | 16 | .82 | .21 |
| .1-.2 | EPA | 31 | .33 | - .50 |
| .1-.2 | Radian | 35 | 1.62 | 4.74 |
| 0-.1 | EPA | 2 | .00 | -2.00 |
| 0-.1 | Radian | 10 | - .86 | .61 |

## TABLE A-3

## SKEWNESS AND KURTOSIS STATISTICS ($NO_x$)

| Test Gas Concentration | Agency | N | Skewness | Kurtosis |
|---|---|---|---|---|
| .4-.5 | EPA | 4 | - .46 | -1.27 |
| .4-.5 | Radian | 4 | - .34 | -1.00 |
| .3-.4 | EPA | 12 | - .39 | - .33 |
| .3-.4 | Radian | 21 | .71 | .02 |
| .2-.3 | EPA | 18 | - .48 | - .61 |
| .2-.3 | Radian | 8 | - .85 | .39 |
| .1-.2 | EPA | 31 | - .10 | - .63 |
| .1-.2 | Radian | 47 | 1.09 | 1.07 |
| 0-.1 | EPA | 7 | - .25 | - .79 |
| 0-.1 | Radian | 6 | 1.35 | .35 |

## TABLE A-4
## SKEWNESS AND KURTOSIS STATISTICS (NO)

| Test Gas Concentration | Agency | N | Skewness | Kurtosis |
|---|---|---|---|---|
| .4-.5 | EPA | 6 | - .84 | - .37 |
| .4-.5 | Radian | 4 | - .07 | -1.14 |
| .3-.4 | EPA | 14 | - .08 | -1.05 |
| .3-.4 | Radian | 23 | .58 | .13 |
| .2-.3 | EPA | 27 | .50 | - .56 |
| .2-.3 | Radian | 8 | - .86 | .76 |
| .1-.2 | EPA | 44 | .21 | - .51 |
| .1-.2 | Radian | 49 | .89 | 2.15 |
| 0-.1 | EPA | 8 | .77 | - .53 |
| 0-.1 | Radian | 6 | .57 | - .07 |

# APPENDIX B
# PROPOSED EXPERIMENTAL DESIGN
# FOR FOLLOW-UP STUDY

Physical questions to be answered spearately for each pollutant:

(1) What effect, if any, can be associated with the time since the last multi-point calibration (MPC)? Are there drifts or do the error variances increase as time increases?

(2) What effect, if any, can be associated with different audit methods, e.g., for gas phase titration versus reverse gas phase titration versus neutral buffered potassium auditing for ozone? How much variation is there among auditing units of the same type?

(3) How much variation is there among Radian-type trailers with respect to the existence and magnitude of drift, etc.?

(4) To what extent do the effects discussed under (1) - (3) repeat from month to month, where each month is controlled by a different MPC?

(5) Can the tentative conclusion of this study that the errors are approximately normally distributed be verified?

(6) Although zero and span values are available for previous days, currently only the current zero and (except for ozone) span values are used for daily autocalibration. Can this procedure be improved upon by employing zero and span values from previous days as well as the current values?

The common theme throughout all of the above concerns is, what is the nature of the random measurement errors, and how should they affect the interpretation and methods of application of the data?

## Data Collection

Define

Y = machine response - test gas concentration

Since the variance is known to change with test gas concentration, it is suggested that entirely separate analyses be performed for a set of test gas concentration intervals, such as those used in this study: 0-.1, .1-.2, .2-.3, .3-.4, and .4-.5 ppm.

Then the value of Y should be obtained just after an MPC and at several subsequent times (say, at 10-day intervals), for two units (if possible) of each type of audit instrument, for each trailer used, for each month, where an MPC is performed at the beginning of each month.

Then, the following data would be available - the variable names associated with the different effects are given in parentheses:

$Y_{ijklm}$ = value for
time i, relative to last MPC, ($T_i$),
audit equipment type j, ($A_j$),
unit k of type j, ($U_{jk}$),
trailer l, ($V_l$), and
monthly time period m ($P_m$).

Obviously, the more data there were, the more confidence one could place in the results. At least two time periods and two trailers should be included, since otherwise random variability from trailer-to-trailer and from month-to-month could not be evaluated at all.

Due to the absence of systematic trailer-to-trailer variances observed in this study, it is felt that this source of variation is not critical and that a meaningful study could be done with as few as two or three trailers. It is recommended that a minimum of three time periods be included, to allow a reasonable chance to evaluate month-to-month variations.

If two units of each of two audit equipment types were used, if four audits per time period per trailer were performed with each unit, if $N_{tr}$ trailers were used, and if $N_{ti}$ time periods were included, then the number of data points $Y_{ijklm}$ available for a given analysis would be

$$16\ N_{tr}N_{ti}$$

Thus, even if $N_{tr}$ and $N_{ti}$ were both two, 64 data points would be available. The suggested three time periods would yield a total of 128 data points, which is many more than were available for each pollutant and test gas concentration in the study reported herein. In view of the variations observed in this study, it is subjectively felt that 128 is an adequate sample size.

Analyses of Trends and Variances

Standard analysis of variance methods would be used to analyze the data described above. A linear model of the following form would be examined:

$$Y_{ijklm} = \mu + T_i + A_j + U_{jk} + V_l + P_m + \text{(interaction terms)}$$

Every attempt would be made to associate physical meaning with the observed effects. Suppose, for example, that the (TV) interaction were significant for j = 3. This would imply that trailer 3 exhibited a drift after the MPC, and $(TV)_{i,3}$ would be the average magnitude of this effect for the $i^{th}$ time point relative to the last MPC. If the other TV terms were insignificant, this would imply that the other trailers did not exhibit such a drift to a measurable extent.

These data would be used to derive a formal decision rule for testing the consistency of an audit point with current trailer operations. This derivation would be similar to the analysis which has already been performed and is reported in Section 2.0, subject to re-examination of individual trailer effects, as is discussed above.

The time effect would be examined closely to reassess the needed frequency of MPC's.

Re-examination of Zero-Span Autocalibration

Notice that

$$E = \sum_{i}\sum_{j}\sum_{k}\sum_{l}\sum_{m} Y^2_{ijklm},$$

the sum of squares of audit point - machine response differences, characterizes the overall magnitude of the discrepancies. If the sum were also extended over the test gas concentration categories, this sum of squares could then be used as an objective function to optimize the policy for zero-span autocalibration for a particular pollutant. Consideration should be given to employing

the analysis of the preceding section to remove observable effects which clearly had nothing to do with the zero-span corrections, such as an effect associated with a particular type of auditing instrumentation.

Combining the data points for different concentrations but for the same pollutant is in contrast with the analysis discussed in the preceding section. While separate analyses for different concentration ranges yields a more detailed error characterization, each zero-span autocalibration applies for all concentrations. Thus, the optimization must employ all of the data for a given pollutant.

Suppose that $Z_n^{(c)}$ and $S_n^{(c)}$ are the zero and span values, respectively, to be used on the $n^{th}$ day, where

$$Z_n^{(c)} = \sum_{i=0}^{P} A_i Z_{n-i}$$

$$S_n^{(c)} = \sum_{i=0}^{P} b_i S_{n-i}$$

and where

$Z_i$ and $S_i$ are the machine responses to the zero and span gases, respectively, on the $i^{th}$ day.

The values of $A_i$ and $b_i$, then, should be chosen to minimize the value of E, subject to the constraints

$$A_i \geq 0 \qquad \sum_{i=0}^{P} A_i = 1$$

$$b_i \geq 0 \qquad \sum_{i=0}^{P} b_i = 1$$

Currently,

$$Z_n^{(c)} = Z_n$$

and

$$S_n^{(c)} = S_n$$

so no benefit of averaging is achieved. The smoothing scheme proposed above would allow averaging of random day-to-day errors and, thus, would hopefully yield more reliable results.

An alternate strategy will be necessary for the case when the required values of $Z_n$ and $S_n$ are not all available.

It should be noted that the audit points used to analyze the trailer errors would also be used in the zero-span analysis. The zero-span data would be obtained as a matter of course while operating the trailers. If the data collection were performed as is discussed at the end of the preceding section, then the total number of audit points for each pollutant would be 128 times the number of test gas concentrations represented in each audit. About 4 or 5 test gas concentrations would be necessary to cover adequately the range from 0 to 5 ppb.

While this may seem like an immoderate number of data points, it must be remembered that sets of four audits are essentially replicate measurements made at the same time with two units each of two types of auditing equipment. Furthermore, regarding the analysis of both this and the preceding sections, it must also be remembered that some of the planned data will inevitably be lost due to system down time.

# APPENDIX C
# SEPTEMBER, 1976, ZERO-SPAN
# AUTOCALIBRATION DATA

TABLE C-1

FOUR-DAY MEAN VALUE OF MACHINE $O_3$ SENSOR RESPONSE TO ZERO GAS VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

| TIME SINCE LAST MULTI-POINT CALIBRATION (DAYS) | TRAILER IDENTIFICATION NUMBER | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | #8 | #10 | #12 | #13 | #14 | #16 | #17 | #18 | #19 |
| 0 | -2.25 | 0.50 | 2.00 | -7.00 | 5.50 | 1.00 | 1.00 | * | 0.50 |
| 4 | 1.75 | +0.00+ | -1.25 | 0.00 | -5.33 | 1.50 | * | -3.00 | -0.25 |
| 8 | 5.50 | 3.50 | -3.67 | -2.50 | -4.50 | 0.00 | * | -2.00 | 0.50 |
| 12 | 2.50 | -1.00 | -3.00 | -4.00 | * | 2.00 | * | -1.00 | -0.25 |
| 16 | 4.00 | 2.00 | -1.50 | -1.50 | * | 2.00 | * | 1.00 | 0.00 |
| 20 | -6.00 | -2.00 | -2.75 | -1.75 | 2.25 | 2.50 | 3.50 | -1.75 | 0.50 |
| 24 | -5.25 | -2.00 | -4.00 | 5.00 | * | 0.00 | 2.00 | 1.50 | 0.25 |
| 28 | -5.75 | -2.25 | -2.75 | * | 0.00+ | 2.00 | -2.33 | -6.00 | -0.75 |

* Indicates points not used.

TABLE C-2

FOUR-DAY STANDARD DEVIATION OF MACHINE $O_3$ SENSOR RESPONSE TO ZERO GAS VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

| TIME SINCE LAST MULTI-POINT CALIBRATION (DAYS) | TRAILER IDENTIFICATION NUMBER | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | #8 | #10 | #12 | #13 | #14 | #16 | #17 | #18 | #19 |
| 0 | 5.19 | 4.12 | 2.31 | 6.08 | 5.80 | 4.36 | 4.83 | * | 1.29 |
| 4 | 2.36 | 0.817 | 3.20 | * | 4.73 | 1.73 | 6.38 | 2.16 | 1.00 |
| 8 | 2.12 | 4.44 | 4.73 | 3.00 | 3.51 | 1.91 | * | 5.72 | 0.50 |
| 12 | 3.19 | 1.16 | * | 3.27 | * | * | 7.12 | 1.41 | 2.65 |
| 16 | 2.83 | 1.41 | 4.95 | 0.71 | * | 1.63 | 5.91 | * | 1.71 |
| 20 | 2.00 | 2.63 | 2.94 | * | 3.61 | 2.83 | 5.86 | 5.29 | * |
| 24 | 0.96 | 0.82 | 3.16 | 4.40 | 2.08 | * | 2.52 | 3.87 | 1.50 |
| 28 | 2.75 | 3.46 | 7.18 | 2.36 | 6.55 | * | 5.35 | 5.38 | 1.26 |

* Indicates points not used.

TABLE C-3

FOUR-DAY MEAN VALUE OF SPAN GAS CONCENTRATION MINUS MACHINE $O_3$ SENSOR RESPONSE VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

| TIME SINCE LAST MULTI-POINT CALIBRATION (DAYS) | TRAILER IDENTIFICATION NUMBER | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | #8 | #10 | #12 | #13 | #14 | #16 | #17 | #18 | #19 |
| 0 | - 5.25 | -25.3 | 11.0 | -13.7 | 2.50 | 3.00 | * | * | 4.50 |
| 4 | - 3.25 | -30.5 | 26.3 | - 8.5 | - 6.33 | 12.3 | 8.25 | - 9.00 | -14.8 |
| 8 | 24.0 | -24.5 | -15.0 | -13.0 | - 6.75 | * | 43.8 | - 3.50 | -37.8 |
| 12 | - 1.75 | -33.0 | 36.0 | -16.0 | * | 6.00 | * | -11.0 | -52.5 |
| 16 | -21.0 | -64.0 | 39.5 | -23.0 | * | 6.50 | * | - 4.0 | -56.5 |
| 20 | - 4.75 | -12.5 | * | * | -29.8 | -11.5 | -12.0 | -10.8 | -16.0 |
| 24 | - 1.75 | - 9.00 | * | 6.50 | -32.7 | -14.0 | -23.3 | 0.50 | - 9.00 |
| 28 | -15.3 | -14.0 | * | * | -13.7 | * | - 8.67 | - 1.00 | - 9.75 |

* Indicates point not used.

TABLE C-4

FOUR-DAY STANDARD DEVIATION OF SPAN GAS CONCENTRATION MINUS MACHINE $O_3$ SENSOR RESPONSE VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

| TIME SINCE LAST MULTI-POINT CALIBRATION (DAYS) | TRAILER IDENTIFICATION NUMBER | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | #8 | #10 | #12 | #13 | #14 | #16 | #17 | #18 | #19 |
| 0 | 5.56 | 7.41 | 14.1 | 12.1 | 5.07 | 14.8 | 14.3 | * | 17.2 |
| 4 | 7.14 | 8.35 | * | 7.05 | 5.51 | 8.19 | 5.89 | 9.76 | 5.26 |
| 8 | * | 8.19 | 14.2 | 9.90 | 17.2 | 8.73 | 16.4 | 13.2 | 15.5 |
| 12 | 5.91 | 5.60 | * | 4.83 | * | * | 5.38 | 8.49 | 16.3 |
| 16 | 13.7 | 12.7 | 3.54 | 14.1 | * | 5.48 | 5.77 | * | 5.97 |
| 20 | 4.50 | 7.94 | 13.6 | * | 4.16 | 9.19 | 2.83 | 3.46 | 12.0 |
| 24 | 4.65 | 6.27 | 6.29 | 5.69 | 6.11 | * | 13.3 | 3.11 | 6.65 |
| 28 | 12.8 | 6.08 | * | * | 17.9 | * | 7.36 | 5.91 | 5.60 |

* Indicates points not used.

TABLE C-5

FOUR-DAY MEAN VALUE OF MACHINE $SO_2$ SENSOR RESPONSE
TO ZERO GAS VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

| TIME SINCE LAST MULTI-POINT CALIBRATION (DAYS) | TRAILER IDENTIFICATION NUMBER | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | #8 | #10 | #12 | #13 | #14 | #16 | #17 | #18 | #19 |
| 0 | 0.00+ | * | -1.75 | * | 1.50 | -1.00 | -1.00 | * | -3.00 |
| 4 | * | -0.50 | -1.50 | -0.75 | 0.00+ | -1.25 | -2.50 | -2.25 | * |
| 8 | * | -1.50 | -1.33 | -1.75 | 1.50 | * | -4.50 | -1.75 | -1.00 |
| 12 | * | -1.00 | -2.00 | -2.00 | 1.75 | -1.00 | -6.00 | -2.50 | -2.50 |
| 16 | -0.50 | * | -2.00 | -2.00 | 1.00 | -0.50 | -6.00 | * | 1.50 |
| 20 | * | 0.25 | -0.75 | 0.50 | -1.00 | * | -1.33 | -3.00 | -6.00 |
| 24 | -0.25 | 0.25 | -1.00 | 2.25 | 0.00+ | -2.00 | 0.00+ | -2.00 | -6.00 |
| 28 | -0.25 | 0.33 | -0.50 | 1.75 | -0.50 | -1.25 | -1.00 | -2.50 | -5.25 |

* Indicates points not used.

TABLE C-6

FOUR-DAY STANDARD DEVIATION OF MACHINE $SO_2$ SENSOR RESPONSE TO ZERO GAS VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

| TIME SINCE LAST MULTI-POINT CALIBRATION (DAYS) | TRAILER IDENTIFICATION NUMBER | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | #8 | #10 | #12 | #13 | #14 | #16 | #17 | #18 | #19 |
| 0 | 0.82 | * | 1.26 | 0.50 | 1.73 | 1.50 | 1.83 | * | 0.50 |
| 4 | * | 0.58 | 1.00 | * | 1.00 | * | 2.00 | 0.96 | 3.46 |
| 8 | * | 0.58 | 1.16 | 1.50 | 0.58 | 1.50 | 1.73 | 0.96 | * |
| 12 | * | * | 1.00 | 1.26 | 0.50 | * | 2.65 | 0.71 | 0.82 |
| 16 | 0.71 | * | * | * | 1.41 | 0.82 | 1.41 | * | 0.50 |
| 20 | * | 0.50 | 0.50 | * | 1.00 | 0.71 | 1.41 | * | 0.64 |
| 24 | 0.50 | 0.50 | * | 0.71 | 2.00 | * | 2.31 | 0.82 | * |
| 28 | 0.50 | 0.58 | 1.29 | 1.26 | 1.73 | * | 1.41 | 0.58 | 2.12 |

* Indicates points not used.

TABLE C-7

FOUR-DAY MEAN VALUE OF SPAN GAS CONCENTRATION MINUS MACHINE $SO_2$ SENSOR RESPONSE VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

| TIME SINCE LAST MULTI-POINT CALIBRATION (DAYS) | TRAILER IDENTIFICATION NUMBER | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | #8 | #10 | #12 | #13 | #14 | #16 | #17 | #18 | #19 |
| 0 | 12.8 | 2.75 | -10.0 | 8.00 | 15.0 | * | 4.75 | 26.0 | -16.8 |
| 4 | 15.3 | 3.00 | 11.0 | 14.0 | - 2.67 | 60.8 | 12.8 | - 3.00 | -20.5 |
| 8 | 18.5 | 2.25 | - 6.33 | 12.5 | - 5.75 | -36.0 | 5.75 | - 4.00 | -30.3 |
| 12 | 24.0 | 5.00 | - 8.00 | 7.25 | -12.8 | -26.3 | 1.50 | - 5.00 | -12.5 |
| 16 | 34.5 | 8.50 | - 6.50 | 46.0 | - 9.50 | -14.5 | 3.50 | - 3.00 | -26.0 |
| 20 | - 6.00 | 5.50 | - 2.50 | - 2.50 | -13.3 | 19.0 | 2.67 | -41.3 | -12.5 |
| 24 | 20.5 | 4.00 | - 3.50 | - 7.00 | -10.00 | 1.00 | 6.00 | - 6.25 | 25.5 |
| 28 | 4.25 | 6.00 | - 0.75 | -54.5 | - 6.25 | 50.0 | 2.75 | -11.3 | 25.0 |

* Indicates points not used.

TABLE C-8

FOUR-DAY STANDARD DEVIATION OF SPAN GAS CONCENTRATION MINUS MACHINE $SO_2$ SENSOR RESPONSE VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

| TIME SINCE LAST MULTI-POINT CALIBRATION (DAYS) | TRAILER IDENTIFICATION NUMBER | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | #8 | #10 | #12 | #13 | #14 | #16 | #17 | #18 | #19 |
| 0 | 14.2 | 2.63 | 7.17 | 7.20 | 36.1 | 52.0 | 0.82 | 1.83 | 8.69 |
| 4 | 10.2 | 2.16 | 38.4 | 9.56 | 2.52 | * | 5.12 | 1.83 | 13.9 |
| 8 | 3.54 | 2.22 | 5.51 | 13.6 | 5.12 | 42.5 | 2.63 | * | 14.7 |
| 12 | 8.04 | 2.45 | * | 9.11 | 1.77 | 18.0 | 2.87 | * | 1.50 |
| 16 | 4.95 | 0.71 | 0.71 | 48.1 | 4.95 | 20.5 | 2.08 | * | 57.5 |
| 20 | 7.12 | 3.32 | 1.92 | 3.54 | 2.52 | * | 0.71 | * | 9.90 |
| 24 | 28.6 | 1.83 | 0.58 | 8.04 | 2.65 | * | 6.43 | 9.74 | 2.52 |
| 28 | 11.1 | 6.08 | 1.50 | 38.7 | 3.69 | * | 2.63 | 6.24 | 51.2 |

* Indicates points not used.

TABLE C-9

FOUR-DAY MEAN VALUE OF MACHINE NO$_x$ SENSOR RESPONSE TO ZERO GAS VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

| TIME SINCE LAST MULTI-POINT CALIBRATION (DAYS) | TRAILER IDENTIFICATION NUMBER | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | #8 | #10 | #12 | #13 | #14 | #16 | #17 | #18 | #19 |
| 0 | 6.50 | -1.00 | 7.00 | 4.67 | 6.25 | 10.3 | 7.50 | * | - 7.25 |
| 4 | 4.50 | 1.00 | 12.5 | 6.25 | 5.00 | 12.8 | 7.50 | 8.5 | - 2.25 |
| 8 | 8.50 | 4.25 | 6.67 | 3.25 | 8.75 | * | 1.00 | 10.8 | * |
| 12 | 11.25 | 3.50 | * | 4.75 | 7.25 | 11.0 | 3.75 | 13.5 | 13.3 |
| 16 | 13.0 | 4.00 | * | 11.5 | 5.00 | 4.50 | 5.00 | 3.00 | 11.5 |
| 20 | 2.00 | -1.75 | 3.25 | 10.3 | 0.33 | 13.0 | 4.00 | 3.75 | - 6.25 |
| 24 | 1.25 | -3.00 | 0.50 | 5.50 | 0.33 | 7.00 | 9.75 | 5.00 | 0.75 |
| 28 | 5.75 | -1.00 | 5.25 | * | 0.50 | * | 5.33 | -0.33 | 0.00+ |

* Indicates points not used.

## TABLE C-10

## FOUR-DAY STANDARD DEVIATION OF MACHINE NO. SENSOR RESPONSE TO ZERO GAS VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

| TIME SINCE LAST MULTI-POINT CALIBRATION (DAYS) | TRAILER IDENTIFICATION NUMBER | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | #8 | #10 | #12 | #13 | #14 | #16 | #17 | #18 | #19 |
| 0 | 9.82 | 1.41 | 7.26 | 4.04 | 3.10 | 9.07 | 3.32 | * | * |
| 4 | 6.46 | 3.46 | * | 4.27 | 5.57 | 8.77 | 3.32 | 3.87 | * |
| 8 | * | 4.27 | 7.02 | 4.35 | 1.50 | * | 5.29 | 2.36 | 1.29 |
| 12 | 4.57 | 2.65 | * | 5.68 | 4.50 | 8.21 | 2.75 | 2.12 | 2.36 |
| 16 | 8.49 | 1.41 | * | * | 7.07 | 6.36 | 1.41 | * | 2.12 |
| 20 | 2.45 | 1.00 | 5.12 | 1.89 | 1.00 | * | 4.97 | 1.26 | 3.86 |
| 24 | 1.89 | 2.16 | 0.58 | 7.19 | 0.58 | * | 3.78 | 0.82 | 2.87 |
| 28 | 8.30 | 1.71 | 3.59 | * | 0.58 | * | 6.81 | 3.22 | 3.74 |

* Indicates points not used.

TABLE C-11

FOUR-DAY MEAN VALUE OF SPAN GAS CONCENTRATION MINUS MACHINE $NO_x$ SENSOR RESPONSE VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

| TIME SINCE LAST MULTI-POINT CALIBRATION (DAYS) | TRAILER IDENTIFICATION NUMBER | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | #8 | #10 | #12 | #13 | #14 | #16 | #17 | #18 | #19 |
| 0 | -9.50 | 4.25 | * | - 1.33 | -36.0 | - 3.33 | 18.8 | 32.5 | 11.3 |
| 4 | -5.25 | -0.25 | * | - 2.50 | 30.0 | - 1.00 | 1.00 | 13.0 | 6.75 |
| 8 | -2.50 | 2.25 | * | - 4.75 | 25.0 | * | 9.00 | 27.3 | 3.25 |
| 12 | 0.50 | 1.75 | 9.00 | - 6.00 | 4.00 | 5.00 | 4.00 | 38.5 | 4.25 |
| 16 | 4.00 | 3.50 | 10.5 | -30.0 | 4.00 | 7.00 | 5.50 | 1.00 | 4.00 |
| 20 | * | -1.00 | - 8.00 | -27.3 | 4.00 | -12.0 | 3.25 | 5.50 | 6.75 |
| 24 | -3.00 | -5.75 | -11.3 | 4.75 | 2.67 | 3.00 | - 2.25 | 3.25 | - 2.00 |
| 28 | -2.25 | -5.00 | - 5.25 | * | - 0.33 | -12.0 | 22.0 | 1.67 | - 2.25 |

* Indicates points not used.

TABLE C-12

FOUR-DAY STANDARD DEVIATION OF SPAN GAS CONCENTRATION MINUS MACHINE NO. SENSOR RESPONSE VERSUS TIME SINCE LAST MULTI-POINT CALIBRATION

| TIME SINCE LAST MULTI-POINT CALIBRATION (DAYS) | TRAILER IDENTIFICATION NUMBER | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | #8 | #10 | #12 | #13 | #14 | #16 | #17 | #18 | #19 |
| 0 | 36.3 | 7.89 | 4.24 | 1.53 | * | 16.6 | 35.9 | * | 13.5 |
| 4 | 4.57 | 2.63 | 27.4 | 3.70 | 27.2 | 10.2 | 3.27 | 7.30 | 15.8 |
| 8 | 2.12 | 2.22 | 7.94 | 3.20 | 4.66 | 5.83 | 8.76 | 2.87 | 4.35 |
| 12 | 6.56 | 1.71 | * | 2.16 | 5.89 | * | 1.83 | 0.71 | 7.59 |
| 16 | 2.83 | 3.54 | 2.12 | 19.8 | 5.66 | 11.6 | 3.54 | * | 7.07 |
| 20 | 1.41 | 2.65 | 7.62 | 19.7 | 3.92 | 9.90 | 4.11 | 3.00 | 5.68 |
| 24 | 2.16 | 1.71 | 3.86 | 4.43 | 3.22 | * | 3.50 | 2.22 | 2.45 |
| 28 | 9.64 | 2.16 | 7.89 | * | 2.31 | * | 6.43 | 0.58 | 6.19 |

* Indicates points not used.

## TABLE C-13
## DATES OF MULTI-POINT CALIBRATIONS PERFORMED IN SEPTEMBER, 1976*

| TRAILER | DATE |
|---|---|
| 8 | 15 |
| 10 | 17** |
| 12 | 13 |
| 13 | 13 |
| 14 | 16 |
| 16 | 11 |
| 17 | 10 |
| 18 | 14 |
| 19 | 12 |

* All of the zero-span data presented in this Appendix and in Section 3 were collected in September, 1976.

**The $SO_2$ multi-point calibration was performed on September 15.